o-, *m*-, and *p*-aminophenyl methyl sulfides were determined by glc analysis carried out using the same column described above and reported before.[2]

The reduction process, as the glc analysis, was shown to be satisfactory (±2%) by the use of synthetic mixtures of pure isomers. Oxidation-nitration composition as isomeric compounds values are an average of three gas chromatographic analysis and the areas are corrected by calculated correction factors.

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Registry No.—Methyl phenyl sulfoxide, 1193-82-4; diphenyl sulfoxide, 945-51-7.

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Reaction of Aromatic Substrates with Sulfonyl Nitrenes[1a]

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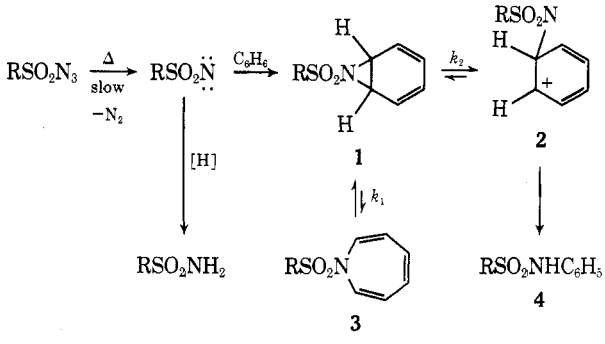
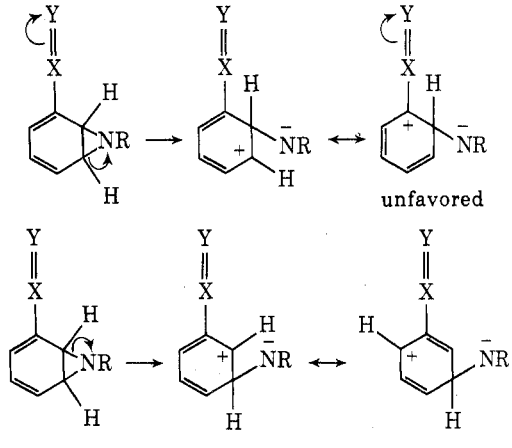
The thermolysis of methanesulfonyl azide in aromatic solvents bearing electron-withdrawing substituents has been studied quantitatively in the presence and absence of compounds known to catalyze singlet → triplet interconversions. The results show that the singlet sulfonyl nitrene formed initially drops to the triplet to a certain extent: the singlet adds to the aromatic nucleus to give a benzaziridine intermediate that ring opens to yield the meta-substituted anilide predominantly. The triplet attacks the nucleus as expected of a highly electrophilic diradical and leads mainly to the ortho isomer. In nitrobenzene, the nitrene behaves only as the electrophilic triplet and, in addition to nitroanilides, yields products in which the nitro group has been displaced.

The thermal decomposition of sulfonyl azides in aromatic solvents, which was first studied by Bertho, Curtius, and Schmidt,[1b] occurs slowly at 120°, is unimolecular,[2] and leads to singlet nitrenes.[3] This is followed by an addition to the aromatic nucleus to give a benzaziridine intermediate (1), with ring opening of the latter to form the observed *N*-sulfonanilides (4)[3] *via* 2 being a relatively fast, thermodynamically controlled process, and ring opening to form the azepine (3) being an even faster kinetically controlled reaction.[4] The unsubstituted primary sulfonamides, products of hydrogen abstraction by the nitrene, are also formed in these reactions.



The isomer ratios and relative reactivities[3] in the reactions of methanesulfonyl nitrene with toluene, anisole, and chlorobenzene could be explained readily on the basis of the above mechanism. Electron-donating substituents facilitate addition to the aromatic nucleus while electron-withdrawing ones slow the addition down. The substituent determines the direction of ring opening 1 → 2 by whether or not it can stabilize the developing positive charge in the aromatic nucleus in the product-, but not rate-, determining step. Since formation of a σ complex is not rate determining, partial rate factors have no physical significance in this reaction[3] and are not considered here.

It would then be predicted that an electron-withdrawing substituent would not only deactivate the nucleus but would also direct the ring opening of the aziridine ring to favor formation of the meta isomer. Confirmation of this



appeared to be forthcoming from studies of the benzenesulfonamidation of methyl benzoate and benzoyl chloride using benzenesulfonyl azide, when the isomer ratios were reported to be ortho, 43%; meta, 54%; para, 3%; and meta, 100%, for these two substrates, respectively, and the total rate ratio $^{CO_2Me}{}_HK = 0.38$.[5] Since these latter data were obtained from fractional distillation experiments and we had found in earlier work[3] that these led to poor quantitative results, it was felt that the reaction of sulfonyl nitrenes with aromatic nuclei bearing electron-withdrawing substituents should be reinvestigated quantitatively using gas–liquid chromatography (glc). Once

Table I
Methanesulfonamidation of Aromatic Substrates

Registry no.	X in C_6H_5X	Overall yield, %	Yield of $CH_3SO_2NH_2$,[a] %	Yield of $CH_3SO_2NHC_6H_4X$,[a] %	Isomer ratio for $CH_3SO_2NHC_6H_4X$, % Ortho	Meta	Para	Total rate ratio ^XH_K
	CH_3[b]	99.5	22.7	76.8	65.4	2.4	32.2	1.86
	OCH_3[b]	70.7	3.8	66.9	55.5	1.2	43.3	2.54
108-90-7	Cl	78.2	13.1	65.1	57.4	0.9	41.7	0.44
93-58-3	CO_2CH_3[b]	26.0	4.6	21.4	64.3	34.4	1.3	0.30
98-95-3	NO_2	17.0	11.7	5.3	55.4	13.4	31.2	c
100-47-0	CN	11.2	5.8	5.4	68.9	31.1	0.0	c
98-08-8	CF_3	51.0	25.8	25.2	53.0	46.1	0.9	0.07

[a] Based on sulfonyl azide. [b] Reference 3. [c] Not determined.

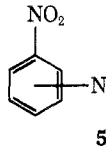
again, in order to facilitate the elution of the reaction products from the column, it was decided to use methanesulfonyl azide instead of benzenesulfonyl azide as the source of the nitrene intermediate. We now report the reaction of methanesulfonyl nitrene with methyl benzoate, benzonitrile, benzotrifluoride, and nitrobenzene.

Decomposition of methanesulfonyl azide in degassed methyl benzoate under nitrogen gave the methyl *N*-methanesulfonylaminobenzoates in an ortho:meta:para ratio of 64.3:34.4:1.3. The corresponding ratio in nitration[6] is 28.3:68.4:3.3, and in free-radical phenylation it is 57:17:25.[7] A polar free radical would be expected to yield a higher proportion of ortho isomer than does the phenyl radical.[8] Methanesulfonamide was isolated as well (4.6%) but no product of addition to the substituent. The total rate ratio (measured by competition experiments) was $^{CO_2Me}{}_HK$ = 0.3. In agreement with the prediction made above the methoxycarbonyl substituent deactivates the ring toward attack by the electrophilic nitrene but, contrary to what was expected for the singlet species, the ortho and not the meta isomer was the main product of attack, though the proportion of meta isomer increased markedly as compared with toluene as substrate (2.4%). This would be consistent with a substitution by the electrophilic triplet sulfonyl nitrene radical. The yield of anilides was much lower than those obtained (65–77%) when an electron-donating substituent was present.[3] Methanesulfonamidation of ethyl benzoate took place similarly but the peaks tailed badly on gas chromatographic analysis and quantitative analysis was not attempted.

Similar results were obtained with benzonitrile and benzotrifluoride (Table I), the yield of sulfonamidation products being quite low (5.4 and 25.2%, respectively) and the ortho isomer being the main product. The proportion of meta isomer was again much higher than when an electron-donating substituent was present and, in the case of benzonitrile, no para-substituted product could be detected.

On going to a substrate bearing an even more electron-withdrawing substituent a dramatic change took place. Using scrupulously degassed reagents a maximum 5.3% yield of nitro-*N*-methanesulfonanilides (**5**) was obtained in

$$MeSO_2N_3 + PhNO_2 \xrightarrow[N_2]{\Delta}$$



$$\xrightarrow{} \underset{\mathbf{5}}{NHSO_2Me} + \underset{\mathbf{6}}{PhOSO_2Me} + \underset{\mathbf{7}}{PhNHSO_2Me} + MeSO_2NH_2$$

the ratio of ortho:meta:para of 55.4:13.4:31.2. This is strikingly similar to the isomer ratio obtained in the homolytic arylation of nitrobenzene using the electrophilic *p*-nitrophenyl radical (ortho:meta:para = 58.15:27).[9] Just as interesting were the other products formed in this reaction in addition to methanesulfonamide, namely phenyl methanesulfonate (**6**) and methanesulfonanilide (**7**). Much tar was also formed.

These results are entirely consistent with an attack of the nitrobenzene ring by triplet electrophilic methanesulfonylnitrene. Displacement of a nitro group by electrophilic free radicals is known. Thus, hydroxyl radicals react with nitrobenzene to give phenol,[10] and displacement of an NO_2 group has been observed in a Pschorr cyclization.[11] Evolution of nitric oxide in the decomposition of sulfonyl azides has been observed[5,12] but not accounted for.

When the reaction was carried out in the presence of air the amount of nitro-*N*-methanesulfonanilide dropped, eventually to zero, with increasing oxygen concentration, and only the ortho isomer could be detected. The yield of **6** was unaffected by the presence of O_2 but that of **7** dropped drastically. Only a small change in the yield of methanesulfonamide was observed (see Experimental Section).

A possible explanation for these observations is as follows. Thermolysis of the sulfonyl azide leads to the singlet electrophilic sulfonyl nitrene, which may add to surrounding aromatic molecules, if the latter are sufficiently reactive, to give aziridine intermediates. If the substrate is unreactive toward attack by an electrophilic singlet the latter has time to drop to the triplet ground state[13] [alternatively, the substituent (or NO in the nitrobenzene reaction) could perhaps catalyze the singlet → triplet conversion (as ethyl acetate may do in the case of cyanonitrene)] which would then attack (not very efficiently) the aromatic nucleus as do other electrophilic free radicals, and the isomer ratio observed would reflect this. The effect of O_2 upon the yields of **5** and **7** is consistent with the interception of a radical before it can react with nitrobenzene. In the presence of radicals, sulfonyl azides can undergo S–N bond cleavage.[14] The formation of **6** may then be rationalized as follows.

$$MeSO_2N_3 + R\cdot \longrightarrow MeSO_2\cdot + RN_3$$

$$MeSO_2\cdot \xrightarrow{[O]} MeSO_3\cdot \longrightarrow \underset{\mathbf{6}}{MeSO_3Ph} + [NO_2\cdot]$$

Oxygen abstraction by $MeSO_2\cdot$ either from nitrobenzene or possibly by disproportionation (but not by reaction with atmospheric oxygen in view of the lack of effect of the latter upon the yield of **6**) finds a parallel in the decomposition of $PhSO_2CHN_2$ in benzene when one of the products is $PhSO_3CH_2SO_2Ph$.[15] The formation of **7** probably involves either displacement of $NO_2\cdot$ by $MeSO_2NH\cdot$ (formed by hydrogen abstraction), or by $MeSO_2N\cdot$ to give $C_6H_5\dot{N}SO_2Me$ which undergoes hydrogen abstraction.

To explain the greatly increased proportion of meta isomer from the reactions with methyl benzoate, benzoni-

Table II
Methanesulfonamidation of Methyl Benzoate and Benzotrifluoride in the Presence of Various Additives

Conditions	Products, % Ortho	Meta	Para	$MeSO_2NHC_6H_4X$	$MeSO_2NH_2$
	A. $PhCO_2Me$				
Sealed tubes under N_2	64.3	34.4	1.3	21.4	4.6
Sealed tubes under air	59.8	38.1	2.0	16.3	5.9
With oxygen bubbled through	55.1	42.6	2.3	20.5	5.3
CCl_4 (20 molar excess)	62.4	35.2	2.4	16.0	*a*
CCl_4 (40 molar excess)	62.9	35.0	2.1	12.9	*a*
CH_2Br_2 (20 molar excess)	56.4	34.9	8.7	2.0	28.3
CH_2Br_2 (40 molar excess)	29.9	57.5	12.6	1.1	44.2
Cobalt (III) acetylacetonate	32.3	63.3	4.4	2.2	*a*
Manganese (II) acetylacetonate	27.3	68.2	4.5	1.3	*a*
Manganese (II) acetylacetonate (trace)	61.4	37.1	1.5	16.6	*a*
$MnCl_2 \cdot 4H_2O$	61.6	36.7	1.67	13.6	*a*
Gattermann copper	56.2	40.5	3.3	5.8	*a*
Iron powder	60.7	37.9	1.4	19.1	*a*
	B. $PhCF_3$				
Degassed under N_2	53.4	45.6	1.0	20.4	21.9
With oxygen	48.0	47.5	4.5	24.4	16.0
CH_2Br_2 (20 molar excess)	34.3	50.0	15.7	0.94	46.5
Copper (II) acetylacetonate	38.2	58.1	3.7	4.3	29.5
Manganese (II) acetylacetonate	43.9	54.1	2.0	4.1	29.0
$Co_2(CO)_8$	31.2	66.8	2.0	2.9	16.1
$Fe_3(CO)_{12}$	30.7	64.0	5.3	0.75	61.5
$Fe(CO)_5$	23.8	69.7	6.5	0.55	53.2

[a] Not determined.

trile, and benzotrifluoride, it is tempting to suggest that two competing processes are operating: (1) the addition of singlet nitrene to give an *N*-sulfonylaziridine intermediate which, on ring opening, gives mainly the meta isomer σ complex as discussed above, and (2) a direct free-radical substitution by triplet electrophilic sulfonyl nitrene, which would lead mainly to the ortho isomer. As the aromatic nucleus becomes more deactivated toward attack by an electrophilic singlet species [$\sigma_p(CO_2Me) = 0.45$; $\sigma_p(CF_3) = 0.54$][16] the latter has time to undergo spin inversion to the triplet to some extent. With nitrobenzene [$\sigma_p(NO_2) = 0.78$][16] this process appears to be complete. The isomer ratios observed for methyl benzoate, benzonitrile, and benzotrifluoride do not conform to either "pure" electrophilic substitution or "pure" radical substitution but rather to a dual mechanism.[17] The total rate ratios (Table I) confirm that these nuclei are deactivated toward electrophilic attack. These ${}^{X}_{H}K$ values must, therefore, be composites of two different mechanistic processes. This receives support as follows.

A good linear relationship is observed for the plot of log ${}^{X}_{H}K$ *vs.* σ_p when X = OCH_3, CH_3, H, and Cl. Much more scatter is observed when log ${}^{X}_{H}K$ is plotted against σ_p^+. The better fit with σ_p than with σ_p^+ is consistent with a transition state resulting from the attack of the aromatic nucleus by a highly reactive species. If σ_p is taken only as a measure of the overall electron-donating or slightly withdrawing ability of the substituent this correlation is understandable. The total rate ratio is, however, a measure of the rate of attack at all the ring positions, and the above linearity with σ_p is not altogether meaningful. On the other hand, the points for methoxycarbonyl and trifluoromethyl are well off this plot (Figure 1). This is understandable not only because of the above duality of mechanisms but also because the relative amount of para isomer in these cases is very low (the main products are the ortho and meta isomers) and σ_p will be a poor measure of the overall reactivity of the nucleus.

In order to obtain more data on this dual mechanism, the methanesulfonamidations of methyl benzoate and benzotrifluoride were carried out in the presence of compounds which are known to facilitate singlet → triplet nitrene conversion.[20] The results of this study are given in Table II.

Methylene bromide is known to be an efficient heavy atom solvent for catalyzing singlet → triplet intersystem crossing of cyanonitrene.[20] Methylene chloride is reported to do the same to carbethoxynitrene.[21] Addition of a large excess of methylene bromide to methyl benzoate and benzotrifluoride before decomposition of the $MeSO_2N_3$ had a dramatic effect both on the relative yields of products and the isomer ratios. The yield of methanesulfonamide increased sharply; that of the *N*-mesylanilines dropped very markedly. The main product of methanesulfonamidation

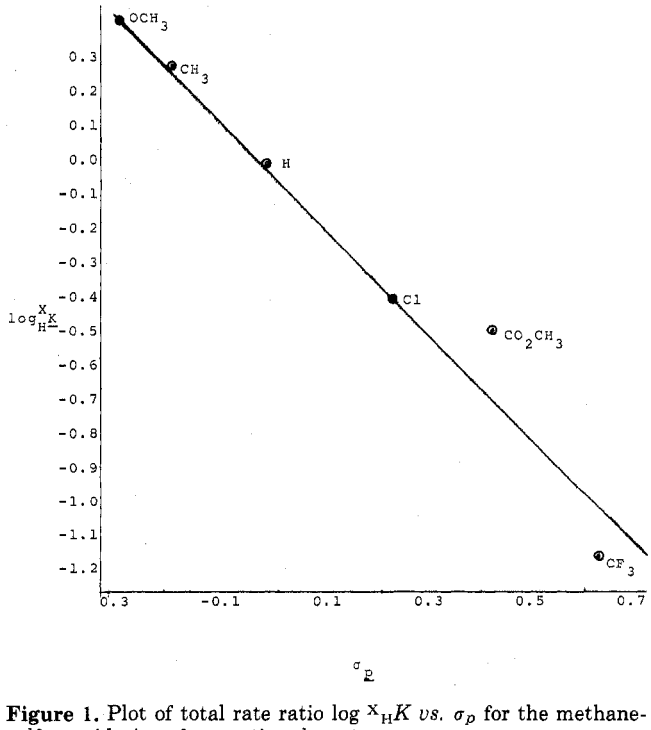


Figure 1. Plot of total rate ratio log ${}^{X}_{H}K$ *vs.* σ_p for the methanesulfonamidation of aromatic substrates.

Table III
Authentic *N*-Mesylanilides $XC_6H_4NHSO_2Me$

Registry no.	X	Yield, %	Mp, °C	Molecular formula	Found, % C	Found, % H	Calcd, % C	Calcd, % H
716-41-6	*o*-CO_2Me	53	90.5–91	$C_9H_{11}NO_4S$	46.83	4.64	47.15	4.84
32087-05-1	*m*-CO_2Me	73	125.5–126	$C_9H_{11}NO_4S$	47.39	5.20	47.15	4.84
50790-28-8	*p*-CO_2Me	63	149.5–150	$C_9H_{11}NO_4S$	47.01	4.82	47.15	4.84
50790-29-9	*o*-CN	50	103	$C_8H_8N_2O_2S$	49.36	4.21	48.98	4.11
50790-30-2	*m*-CN	65	154.5–155	$C_8H_8N_2O_2S$	48.99	4.36	48.98	4.11
36268-67-4	*p*-CN	75	197.5	$C_8H_8N_2O_2S$	49.22	4.22	48.98	4.11
50790-31-3	*o*-CF_3	68	79–80	$C_8H_8F_3NO_2S$	40.55	3.41	40.17	3.37
50790-32-4	*p*-CF_3	65	127–128	$C_8H_8F_3NO_2S$	40.22	3.54	40.17	3.37

is now the meta isomer, as predicted on the basis of an attack of the nucleus by a singlet species. That CH_2Br_2 was a very efficient hydrogen donor was shown by carrying out the decomposition of the azide in this solvent alone. A very clean reaction (unlike the ones in aromatic solvents) occurred to give a 93% yield of methanesulfonamide. These results can be readily interpreted as follows. Methylene bromide catalyzes some intersystem crossing of singlet to triplet, and triplet sulfonyl nitrene hydrogen-abstracts very efficiently from CH_2Br_2 to give $MeSO_2NH_2$. Remaining singlet nitrene does not and adds to the aromatic solvent as predicted above to give mainly the meta-substituted anilide.

When the decompositions were carried out in the presence of copper(II), manganese(II), and cobalt(III) acetylacetonates instead of methylene bromide again the yields of "substitution" products decreased enormously and the relative amount of meta isomer increased at the expense of ortho isomer as the amount of added complex was increased. The transition metal complexes appear to catalyze the singlet → triplet conversion and to trap the triplet in the form of intractable materials (the amorphous products and tars were found to contain transition metal). What is left of the singlet adds to the aromatic substrate as before. When the decompositions in benzotrifluoride were carried out in the presence of $Fe(CO)_5$, $Fe_3(CO)_{12}$, or $Co_2(CO)_8$ an even greater increase in the proportion of meta relative to ortho isomer was observed and, in these cases, when azide was present in excess over transition metal carbonyl, novel nitrene–metal complexes were isolated as amorphous solids. These will form the subject of a forthcoming publication. Manganous chloride, copper, and iron, all of which were insoluble in the reaction medium, had little effect upon the product ratio, as did carbon tetrachloride in 40-molar excess. These results are, therefore, consistent with the intermediacy of both singlet and triplet sulfonyl nitrenes in these unreactive aromatic solvents.

As discussed above, triplet sulfonyl nitrene abstracts hydrogen efficiently from aliphatic solvents, and it appears that metal-complexed sulfonyl nitrenes can do likewise from both aliphatic and aromatic solvents (see above, ref 22). It has been argued, however, that free triplet sulfonyl nitrenes do not abstract hydrogen efficiently from aromatic solvents.[3,22] Breslow and Edwards found that *m*-dinitrobenzene caused the amount of insertion of *n*-octadecyloxycarbonyl nitrene into cyclohexane to increase at the expense of hydrogen-abstraction product and this was attributed to trapping by *m*-dinitrobenzene of the radicals catalyzing singlet → triplet transitions.[23] Addition of excess *m*-dinitrobenzene to methanesulfonyl azide in benzene before thermolysis led to a decrease in the yields of *both* methanesulfonamide *and* *N*-mesylaniline and, indeed, the ratio of amide to anilide *increased* slightly (from 1:4.7 to 1:3.8) upon addition of *m*-dinitrobenzene. This supports our belief that both products in benzene arise from the singlet species; the lower yields obtained in the presence of *m*-dinitrobenzene must reflect a reaction of the nitrene with the nitro compound which is present in large excess.

Experimental Section

Melting points are uncorrected. Nmr spectra were recorded on a 100-MHz instrument.

Reagents. Reagent-grade solvents were purified by standard techniques and kept over drying agent. They were distilled just prior to use. Methanesulfonyl azide was fractionally distilled behind a safety shield and stored in a desiccator at 0°.

Authentic Mesylanilides. These were prepared from the appropriate aniline, methanesulfonyl chloride, and dry pyridine with or without benzene as solvent. The properties of the new mesylanilides so obtained are given in Table III. The other anilides had the properties described in the literature.

General Procedure for the Decomposition of Methanesulfonyl Azide in Aromatic Solvents. All thermolyses were carried out in glass bombs which were stirred and immersed in a thermostated bath at 120°. The initial reaction solution was degassed by evacuating the frozen solution and thawing and repeating this procedure a number of times. The decompositions were allowed to proceed for 48–72 hr, the mixture was cooled to room temperature and filtered, and the insoluble black material was washed with hot acetone, benzene, or acetonitrile. The combined washings and filtrates were fractionally distilled through a Vigreux column and the solvent distillates were checked by gas chromatography to ensure that none of the products codistilled. The concentrated reaction mixtures were analyzed directly by glc after the addition of the appropriate internal standard. A number of synthetic mixtures were analyzed, under the same conditions to check the accuracy of the method.

Methanesulfonamidation of Degassed Methyl Benzoate. The only products detected by glc were methanesulfonamide and the methyl *o*-, *m*-, and *p*-methanesulfonamidobenzoates. These were collected and identified by comparing their ir spectra and melting points with those of authentic samples.

For the quantitative analyses, methanesulfonyl azide (0.15 g) was decomposed as described above in a 50-molar excess of methyl benzoate. The isomerides could be analyzed either on an 8.5 ft × 0.25 in. column packed with Apiezon N (25%) on Chromosorb W (60–80 mesh) and a column temperature of 250° and a He flow rate of 60 ml/min, or on an 8.25 ft × 0.25 in. column of Apiezon L (25%) on Gas-Chrom P (100–120 mesh) at 230° and a flow rate of 100 ml/min. *p*-Methanesulfonyltoluidide was used as the internal standard. Methanesulfonamide was separately analyzed on a 6 ft × 0.25 in. column packed with precipitated asphalt (25%) on Chromosorb W at 180° and a He flow rate of 85 ml/min (*p*-chloronitrobenzene as internal standard). The mean of three runs gave the following results: methanesulfonamide, 4.62 ± 0.6%; methyl *N*-methanesulfonamidobenzoate, 21.4 ± 0.6% (isomer ratios ortho, 64.3 ± 0.7%; meta, 34.4 ± 0.5%; para, 1.3 ± 0.2%); overall yield based on azide, 26.0 ± 1.0%.

Competitive runs between benzene and methyl benzoate were carried out by decomposing the azide in the mixed solvents in the molar ratio azide:benzene:methyl benzoate of 1:50:50. The products were analyzed on the above Apiezon N on Chromosorb W column. Analysis of two synthetic mixtures confirmed the accuracy of the method. The total rate ratio ${}^{CO_2Me}{}_HK$ thus obtained (average of three runs) was 0.30 ± 0.01.

Methanesulfonamidation of Methyl Benzoate in the Presence of Oxygen. The above reaction was repeated under two different sets of conditions: (a) in a sealed bomb under air and (b)

under reflux with oxygen being bubbled through the solution at 120°. The results are given in Table II.

Methanesulfonamidation of Benzonitrile. Only methanesulfonamide and *o*- and *m*-cyano-*N*-methanesulfonanilides were formed and isolated. No *p*-cyano-*N*-methanesulfonanilide could be detected, so that if any is formed it must be present to the extent of less than 3% of the isomerides.

Quantitative analysis for methanesulfonamide was carried out as above while the *o*- and *m*-cyano derivatives were analyzed on the Apiezon L on Gas-Chrom P column described above using 1,2-diphenoxyethane as the internal standard. Synthetic mixtures were also analyzed as before. The yields of products were follow: methanesulfonanilides, 5.7 ± 0.5%; cyano-*N*-methanesulfonanilides, 5.4 ± 0.18% (isomer ratio ortho, 68.9 ± 0.25%; meta, 31.1 ± 0.22%); overall yield based on azide, 11.1 ± 0.75%.

Methanesulfonamidation of Benzotrifluoride. Methanesulfonamide and the three isomeric mesylaminobenzotrifluorides were isolated and characterized. Isomer ratios were determined on a 10 ft × 0.25 in. Apiezon L (25%) on Anakchrom ABS (60–70 mesh) column at 212° and a 60 ml/min He flow rate using benzophenone as the internal standard. The averages of five runs follow: methanesulfonamide, 25.8 ± 3.6%; mesylaminobenzotrifluorides, 25.2 ± 1.3% (isomer ratio ortho, 53.0%, meta, 46.1%; para, 0.9%); overall yield, 51.0 ± 1.7%.

A competitive reaction was carried out using a methanesulfonyl azide:benzene:benzotrifluoride molar ratio of 1:20:20. The products were analyzed on a 10 ft × 3/16 in. Apiezon L (25%) on Chromosorb W (60–200 mesh) column at 225° using benzophenone as the internal standard. The total rate ratio $[^{CF_3}{}_HK]$ thus obtained was 0.06 (average of four runs).

Methanesulfonamidation of Degassed Nitrobenzene. Qualitative Analysis. The thoroughly degassed solution was thermolyzed and the products were analyzed by glc. Methanesulfonamide and the nitro-*N*-methanesulfonanilides were characterized but, in addition, two more peaks were observed. These were collected and their infrared spectra and melting points were compared with those of authentic *N*-methanesulfonanilide, mp 101°, and phenyl methanesulfonate, mp 59–59.5°, and were found to be identical with these.

Quantitative Analysis. Methanesulfonyl azide (0.06 g) in a 50-molar excess of nitrobenzene was thoroughly degassed and decomposed under dry, oxygen-free nitrogen. Methanesulfonamide, methanesulfonanilide, and phenyl methanesulfonate were estimated using the 8.5 ft × 0.25 in. Apiezon N (25%) on Chromosorb W (60–80 mesh) column at 190°, while the isomeric nitro-*N*-methanesulfonanilides were estimated using a 3 ft × 0.25 in. column packed with Apiezon L (20%) on Gas-Chrom P (100–200 mesh) at 195° and a He flow rate of 68 ml/min. Biphenyl was used as the internal standard in both cases. Synthetic mixtures were also analyzed in this way. The results of three runs are as follows: methanesulfonamide, 11.7 ± 1.0%; phenyl methanesulfonate, 2.5 ± 0.5%; methanesulfonanilide, 18.6 ± 0.4; nitro-*N*-methanesulfonanilides, 5.3 ± 1.4% (isomer ratio ortho, 55.4%; meta, 13.4%; para, 31.2%); overall yield based on azide, 38.15 ± 3.0%.

Methanesulfonamidation of Nitrobenzene in the Presence of Oxygen. The above reaction was repeated under three different sets of conditions: (a) in undegassed nitrobenzene in a tube sealed under an air atmosphere; (b) under reflux open to the air at 120°; and (c) under reflux with oxygen being bubbled through the solution at 120°. The yields of products are summarized below. No *m*- or *p*-nitro-*N*-mesylanilide could be detected by glc under these conditions.

Conditions	Yield, % $MeSO_2NH_2$	$PhOSO_2Me$	$PhNHSO_2Me$	o-$NO_2C_6H_4NHSO_2Me$	Σ, %
a	10.9 ± 0.6	2.1 ± 0.2	15.2 ± 0.7	3.0 ± 0.2	31.2
b	9.9 ± 0.7	2.6 ± 0.6	4.5 ± 0.25	2.0	19.0
c	7.5 ± 0.25	2.5 ± 0.07	0.3 ± 0.02	0.0	10.3

Methanesulfonamidation of Benzene in Methylene Bromide. A solution of methanesulfonyl azide (0.3 g, 0.0025 mol) in a 4-molar (1 ml) or a 20-molar (5 ml) excess of benzene was diluted with a 100-molar excess of methylene bromide (17 ml) and the solutions were thermolyzed at 120° under N_2 in a sealed bomb. The products were methanesulfonamide and methanesulfonanilide; no biphenyl was detected. The quantitative analysis were carried out as described earlier.[3]

Molar ratio of azide:benzene: CH_2Br_2	$MeSO_2NH_2$, %	$MeSO_2NHPh$, %	Σ, %
1:4:100	90.95 ± 0.5	1.1 ± 0.3	92
1:20:100	69.8 ± 2.0	2.8 ± 0.03	72.6

Decomposition of Methanesulfonyl Azide in Methylene Bromide. Methanesulfonyl azide (0.3 g) was decomposed in methylene bromide (17 ml) at 120° to give methanesulfonamide (93%) in a very clean reaction.

Methanesulfonamidation of Benzene in the Presence of *m*-Dinitrobenzene. Methanesulfonyl azide (0.3 g) was decomposed in benzene (12.5 ml) containing *m*-dinitrobenzene (0.4 g, 0.003 mol). Methanesulfonamide (7.4 ± 0.1%) and *N*-methanesulfonanilide (34.8 ± 0.6%) were obtained. No biphenyl was detected.

Effect of Diluent and Additives upon Reaction of Methanesulfonyl Azide with Methyl Benzoate. Methylene Bromide. Methanesulfonyl azide (0.3 g) in methyl benzoate (6.8 g) was diluted with 20-molar (3.45 ml) or 40-molar (6.9 ml) excesses of methylene bromide and the thermolyses were carried out as usual. Since the isomeric methane sulfonamidobenzoates were formed in such small amounts, a large percentage error (estimated ±10%) may be introduced in the peak area measurements and was allowed for.

Carbon Tetrachloride. The reaction was repeated but using CCl_4 as the diluent. Methanesulfonamide was the main product but its yield was not determined.

In the Presence of Cobalt(III) Acetylacetonate. Methanesulfonyl azide (0.6 g) was decomposed in a 50-molar excess of methyl benzoate in the presence of cobalt(III) acetylacetonate (0.13–0.18 g) at 120°. A blank run in the absence of azide indicated that the metal complex did not give any isolable products with the benzoate. The overall yield of methyl *N*-methanesulfonamidobenzoates was 2.2% and the isomer ratio was ortho, 32.3; meta, 63.3; para, 4.4. The decompositions in the presence of other transition-metal compounds were carried out and analyzed similarly. The results of these reactions and of the ones of the similar decomposition of $MeSO_2N_3$ in benzotrifluoride in the presence of transition-metal compounds are collected and summarized in Table II.

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Registry No.—Methanesulfonyl azide, 1516-70-7; benzene, 71-43-2.

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Reaction of 3-[2′-Tetrahydropyranyl(furanyl)thio]indole with Silver Ion

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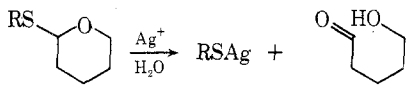
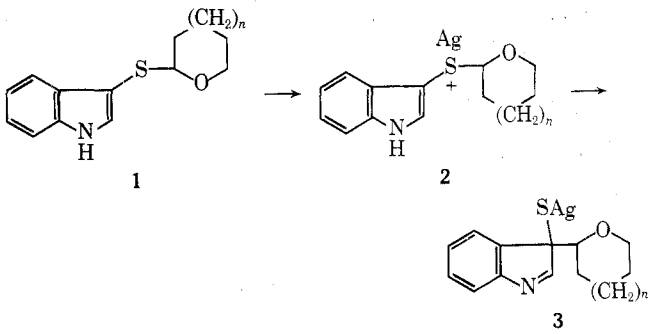
When 3-(2′-tetrahydropyranylthio)indole is treated with 1 equiv of silver ion in aqueous methanol, the silver salt of 3-thioindole and 5-hydroxyvaleraldehyde are produced quantitatively. If the reaction is carried out in an aprotic solvent (toluene, tetrahydrofuran), rearrangements occur to produce low yields of products in which the cyclic ether moiety is bonded to N-1 or C-2 of the indole nucleus. The reactions are envisaged as involving collapse of an initially formed adduct, in which silver ion is bound to sulfur, to release a cyclic ether oxonium ion which undergoes further reaction. Formation of the 1-tetrahydropyranyl(furanyl) compound is envisaged as involving intermolecular formation of 1-tetrahydropyranyl(furanyl)-3-tetrahydropyranyl(furanyl)thioindole which, *via* a silver ion adduct, loses the cyclic ether moiety from sulfur. It is suggested that the C-2-substituted compound may arise by a process in which the cyclic ether moiety is first bonded to C-3 of the indole nucleus followed by migration to C-2.

Reaction of 3-[2′-Tetrahydropyranyl(furanyl)thio]indole with Silver Ion. In connection with studies directed toward achieving new C-nucleoside (*e.g.*, formycin, pseudouridine, pyrazomycin)[1] syntheses, an investigation of the reactions of silver ion with 3-(2′-tetrahydropyranylthio)indole (**1a**) and 3-(2′-tetrahydrofuranylthio)indole (**1b**) was undertaken. Holland and Cohen[2] discovered that the sulfur–hemiacetal linkage is cleaved readily by silver ion in aqueous solution to yield quantitatively a silver mercaptide and a hydroxy aldehyde.



The present study was undertaken in anticipation that, in the absence of a protic solvent, a 1,2 shift from sulfur to carbon[3] might occur.



a, $n = 1$
b, $n = 0$

In accordance with the results of Holland and Cohen,[2] treatment of 3-(2′-tetrahydropyranylthio)indole (**1a**) with aqueous silver nitrate at room temperature resulted in the immediate precipitation of a quantitative yield of the silver salt of 3-thioindole[4] and 5-hydroxyvaleraldehyde, isolated as the corresponding 2,4-dinitrophenylhydrazone.[5] When equimolar amounts of **1a** and silver perchlorate (chosen because of its availability in anhydrous form, its solubility in organic solvents, and the low nucleophilicity of the perchlorate ion) were combined in benzene at room temperature a precipitate was formed which darkened (decomposed) quickly. Evidence consistent with the formulation of this precipitate as the coordination compound **2a** was obtained from two additional experiments. When **1a** and silver perchlorate were mixed in pyridine at room temperature no reaction occurred, indicating that the affinity of pyridine for silver ion prevents its coordination with the sulfur of **1a**. When the reactants were combined in toluene at −78° a colorless precipitate accounting for two-thirds of added reactants formed immediately. Addition of pyridine to the reaction mixture at this point caused the precipitate to dissolve with quantitative regeneration of the starting material, **1a**, indicating that the precipitate was not a product involving cleavage or rearrangement of the organic reactant. However, if the reaction mixture in toluene was allowed to warm in the absence of added pyridine, the original precipitate decomposed and pyridine was no longer capable of removing the silver, indicating that the silver ion was present as a mercaptide.

In addition to providing evidence consistent with the formation of coordination compound **2**, these experiments illustrate the extent to which the activity of silver ion is influenced by its interaction with solvent. After evaluation of a number of solvents, tetrahydrofuran was selected for use in the remainder of this study.

At −78° in tetrahydrofuran, no evidence for the reaction of **1a** with silver perchlorate was obtained. At higher temperatures (−15 to 25°) **1a** underwent reaction presumably *via* the intermediacy of complex **2a**, which, unlike its behavior in benzene and toluene, appears to be soluble in tetrahydrofuran. In contrast, 3-(2′-tetrahydrofuranylthio)-indole (**1b**) reacted in the presence of silver ion even at −78°. Except for these differences in affinity for coordination and reaction rate (which parallel the behavior of 2-*O*-alkyl acetals of tetrahydropyran and tetrahydrofuran toward acid-catalyzed hydrolysis),[6,7] the reactions of **1a** and **1b** with silver perchlorate in tetrahydrofuran were similar.

Silver ion mediated decomposition of **1a** or **1b** in tetrahydrofuran produced heterogeneous precipitates which, in favorable instances, accounted for essentially all of the