Sensitized Photolyses of Methanesulfonyl Azide in Hydrocarbons

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The sensitized photolyses of methanesulfonyl azide (1) in hydrocarbons gave N-substituted methanesulfonamides (4) and methanesulfonamide, although the former had been formed via the singlet sulfonylnitrene and not via the triplet. These sensitized photolyses showed a tertiary/secondary ratio of 18.2 for the insertion regioselectivity toward C–H bonds in 2-methylbutane. The photolyses of 1 in *cis*- and *trans*-1,4-dimethylcyclohexanes led to nonstereospecific formation of 4, respectively, in contrast to the direct photolyses of 1. In the sensitized photolyses, 4 is formed not by a nitrene mechanism, but by a mechanism involving an intermediate, $CH_3SO_2\dot{N}_3H$.

There is much interest in the electronic multiplicities of nitrenes in relation to their insertion into C–H bonds of saturated hydrocarbons. Phenylnitrene inserted only via the triplet,[2] cyanonitrene inserted via both the singlet and the triplet,[3] and alkoxycarbonylnitrenes inserted only via the singlet.[4–7] For the ethers, however, it was found that insertion of ethoxycarbonylnitrene into their α C–H bonds proceeded via both the singlet and the triplet.[8–10]

Methanesulfonylnitrene, generated by the thermolysis or the photolysis of methanesulfonyl azide (1), was less regioselective than the other nitrenes for the insertion in primary, secondary, and tertiary C–H bonds of hydrocarbons.[11] The insertion has been shown to proceed with only the singlet from the stereochemical point of view: the sulfonylnitrene inserted stereospecifically into the tertiary C–H bonds of *cis*- and *trans*-1,4[12]- or 1,2[13]-dimethylcyclohexanes.

In these photolyses of 1 by earlier investigators, a low-pressure mercury lamp, which can excite the azide directly, has been employed. No report on the sensitized photolysis of 1 has been made except the photolysis in isopropyl alcohol, in which the hydrogen abstraction product was quantitatively obtained.[14] The triplet-sensitized photolyses of 1 in hydrocarbons gave the insertion products accompanied by the hydrogen abstraction product. This paper deals with the photosensitized decomposition of 1, describing the formation of the insertion and abstraction products which proceeds via a mechanism different from the nitrene mechanism advanced in the reaction with hydrocarbon C–H bonds.

Results and Discussion

A 1,2-dichloroethane solution of methanesulfonyl azide (1) and a hydrocarbon in the presence of acetophenone was irradiated by light from a high-pressure mercury lamp under an atmosphere of nitrogen (Scheme I). A circulating 1.5 M $CuSO_4$ aqueous solution was provided as a filter. The presence of the filter completely inhibited the direct excitation of 1. The yields of the products are listed in Table I.

$$\underset{1}{CH_3SO_2N_3} + R\text{–}H \xrightarrow[>3000\ \text{Å},\ -N_2]{\text{sensitization}} \underset{4}{CH_3SO_2NHR} + \underset{5}{CH_3SO_2NH_2}$$

R = hydrocarbon residue

Each of the reactions gave N-substituted mathanesulfonamides (4) and methanesulfonamide (5). Product 4 corresponds formally to that resulting from the insertion of singlet methanesulfonylnitrene into the C–H bonds. The formation of 4 under the present condition means that a reactive species other than the singlet nitrene should be involved in the insertion reaction. In the reaction with 2-methylbutane, the reaction products with the tertiary and the secondary C–H bonds ($4B_1$ and $4B_2$, see Table I) were isolated, but those with the primary ones were not detected. On the other hand, the direct photolysis of 1 gave four isomeric insertion products resulting from attack on all the primary, secondary, and tertiary C–H bonds.[11] The relative reactivities of reactive species 2 (Scheme I) toward C–H bonds were compared with those of singlet methanesulfonylnitrene, generated by direct photolysis[10] or thermolysis.[13] The data are displayed in Table II. Reactive species 2 was significantly a more selective intermediate than the singlet nitrene toward the C–H bonds of hydrocarbons. In the reactions with 2-methylbutane and 2,3-dimethylbutane, the lack of detection of the products with the primary C–H bonds is due to the high selectivity of 2. The highly selective insertion shows that 2 has a radical character. Then, different paths leading to 4 are considerable, as shown in eq 7–9 in Scheme I.

Scheme I

Excitation

$$CH_3COC_6h_5 \xrightarrow[>3000\ \text{Å}]{\text{photosensitization}} CH_3COC_6H_5{}^t \quad (1)$$

Energy transfer

$$\underset{1}{CH_3COC_6H_5{}^t} + CH_3SO_2N_3 \rightarrow CH_3COC_6H_5 + \underset{2}{CH_3SO_2N_3{}^t} \quad (2)$$

Abstraction

$$CH_3COC_6H_5{}^t + RH \rightarrow CH_3\dot{C}(OH)C_6H_5 + \cdot R \quad (3)$$

$$CH_3SO_2N_3{}^t \xrightarrow{-N_2} CH_3SO_2\dot{N}\cdot{}^t \xrightarrow{RH} \underset{6}{CH_3SO_2\dot{N}H} + \cdot R \quad (4)$$

$$2 \xrightarrow{RH} \underset{7}{CH_3SO_2NH\text{–}\dot{N}_2} + \cdot R \xrightarrow{-N_2} \underset{6}{CH_3SO_2\dot{N}H} + \cdot R \quad (5)$$

Path leading to 5

$$\underset{6}{CH_3SO_2\dot{N}H} + RH \rightarrow \underset{5}{CH_3SO_2NH_2} + \cdot R \quad (6)$$

Path leading to 4

$$CH_3SO_2\dot{N}H + \cdot R \rightarrow \underset{4}{CH_3SO_2NHR} \quad (7)$$

$$\left.\begin{aligned} \cdot R + CH_3SO_2N_3 &\rightarrow CH_3SO_2\dot{N}R + N_2 \\ CH_3SO_2\dot{N}R + RH &\rightarrow \underset{4}{CH_3SO_2NHR} + \cdot R \end{aligned}\right\} \quad (8)$$

$$\underset{7}{CH_3SO_2NH\text{–}\dot{N}_2} + \cdot R \rightarrow \underset{4}{CH_3SO_2NHR} + N_2 \quad (9)$$

First, a triplet sulfonylnitrene is the most probable intermediate (eq 4 followed by eq 7). The sensitized photolyses of 1 were carried out in *cis*- or *trans*-1,4-dimethylcyclohexane (*cis*-3 and *trans*-3, see Table III) diluted with 1,2-dichloroethane. The results are listed in Table III, compared with those of the direct photolyses of 1.[12]

The reaction of 1 with either *cis*-3 or *trans*-3 gave a mixture of *cis*-4 and *trans*-4 (stereoisomers); the reaction was completely nonstereospecific. On the contrary, the direct photolyses of 1 gave only one tertiary sulfonamide in spite of the presence of the triplet nitrene derived from the singlet.

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Table I. Sensitized Photolyses of 1 in Hydrocarbons

Hydrocarbon (3)	Product,[a] % 4		RNH_2 (5)
Cyclohexane	c-$C_6H_{11}NHR$[b] **A**, 17.8		14.5
$(CH_3)_2CHCH_2$-CH_3	$Ch_3)_2C(NHR)$-$CH(CH_3)_2$ **B_1**, 11.3	$(CH_3)_2CHCH$-$(NHR)CH_3$ **B_2**, 1.3	23.6
$(CH_3)_2CHCH$-$(CH_3)_2$	$(CH_3)_2C(NHR)$-$CH(CH_3)_2$ **C**, 12.2		26.3

[a] Calculated on the basis of the azide used. [b] R = SO_2CH_3.

Table II. Relative Reactivities of 2 and Methanesulfonylnitrene toward the C–H Bonds of 2-Methylbutane

	Product		
	$4B_1$	**$4B_2$**	C_4H_9–CH_2-NHR[a]
Type of C–H bond	3°	2°	1°
Relative reactivity:[b] sensitized	18.2	1	
direct[c]	2.3	1	0.24
thermolysis[d]	2.6	1	0.45

[a] R = SO_2CH_3. [b] Relative reactivities are given per secondary C–H bond. [c] Calculated from the data in ref 11. [d] Formed by decomposition at 150 °C in 1,4-dimethylpentane.[13]

Breslow et al. also reported that the insertion of the nitrene, generated by thermolysis, into the tertiary C–H bonds of *cis*- and *trans*-1,2-dimethylcyclohexanes proceeded stereospecifically.[13] Thus, it is concluded that the triplet nitrene does not insert into the C–H bonds of saturated hydrocarbons. Therefore, the nonstereospecific formation of *cis*-**4** or *trans*-**4** in the sensitized photolyses means that neither the singlet nitrene nor the triplet nitrene takes part in the formation of **4**. As an alternative, **4** may be formed via a mechanism shown in eq 8 from the facts that sulfonyl azides have a tendency to undergo induced decomposition by free radicals.[15] But the formation of **4** by such induced decomposition should be ruled out because the radical necessary to cause the induced decomposition is also produced concomitantly by the formation of **6** in the direct photolyses which lead to the formation of **4** stereospecifically. As a third alternative, the excited triplet azide leading to radical **7** is plausible as shown in eq 9. As for the triplet azide, Lwowski and Mattingly[16] reported the sensitized photolysis of ethyl azidoformate in cyclohexene; the excited triplet azide reacted with the solvent to give an abstraction product (urethane) without first decomposing to a triplet nitrene species because of the absence of the nitrene adduct in the cyclohexene. A tentative mechanism involving the triplet azide in the sensitized photolyses of methanesulfonyl azide may be as follows. Radical **6**, which is derived from the triplet nitrene and from radical **7**, gives only the abstraction product (**5**) without recombination with a hydrocarbon radical (·R). On the other hand, the amino radicals derived from triplet phenylnitrene[2] and triplet cyanonitrene[3] are able to recombine with hydrocarbon radicals to give the insertion products. Both amino radicals can be stabilized by resonance between the nitrogen atom and the phenyl or the cyano group, whereas no resonance stabilization, other than that involving d-orbital expansion on the sulfur atom, is available to radical **6**. However, radical **7**, derived from the triplet azide, would be stabilized by the nitrogen atoms in comparison with **6**. The long-lived radical **7**, stabilized by resonance, can thus recombine with the hydrocarbon radical to give **4** with evolution of nitrogen.

Experimental Section

IR spectra were recorded on Hitachi EP-S and Nippon Bunko (Jasco) Model A-3 photometers, and NMR spectra were taken on Hitachi R-20 and R-24 instruments, using tetramethylsilane as an internal standard. VPC was done on Shimdzu GC-2C and Nippon Denshi (JEOL) JGC 20K units, employing the following as absorbents: (A) 20% Apiezon M on Neopak 1A (60–80 mesh); (B) 20% Ucon Oil 5 HB 2000 on Celite (60–80 mesh); (C) 10% polyethylene glycol succinate on Neopak 1A (60–80 mesh). The products were separated by VPC, and the structures of the products were determined by means of elemental analyses and by measurements of the IR and NMR spectra. The structures of some of the products were determined by comparing their IR and NMR spectra with those of authentic samples. The quantitative analyses of the products by VPC and tests for the stability of each product during VPC analysis have been described in a previous paper.[17]

Materials. Methanesulfonyl azide (**1**) was prepared by the method of Reagan and Nickon.[14] Cyclohexane, 2-methylbutane, 2,3-dimethylbutane, and 1,2-dichloroethane were used after the commercial reagents had been purified according to the published directions.[18] Analytical grade acetophenone was used without further purification.

cis- and *trans*-1,4-Dimethylcyclohexanes (*cis*-**3** and *trans*-**3**) were prepared by the method of Feulgen.[19] A mixture of *p*-xylene (212 g, 2 mol) and acetic acid (180 g) was stirred in the presence of platinum black catalyst (2 g) and hydrogen at room temperature under ordinary pressure. The solution, separated from the catalyst by distillation at about 50 °C under reduced pressure, was washed with a 10% sodium carbonate solution and water and dried over potassium carbonate. A complete separation of the dimethylcyclohexanes into their geometric isomers was accomplished by repeated fractional distillation: *trans*-**3**, 119 °C; *cis*-**3**, 124 °C.[20] The purity of each isomer was checked on column A: column temperature, 90 °C; carrier gas, H_2, 30 mL/min; retention time, 10 min for *trans*-**3** and 12 min for *cis*-**3**. This separation gave a molar ratio of *cis*-**3** to *trans*-**3** of 3:1. No photochemical isomerization between *cis*-**3** and *trans*-**3** was observed under the conditions of these experiments.

N-Cyclohexylmethanesulfonamide (**4A**) was prepared from cyclohexylamine and methanesulfonyl chloride in a way similar to the preparation of cyclohexylurethane:[16] mp 103 °C; IR (Nujol) 3230 (NH), 1310 and 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 5.56 (brd s, 1, NH), 6.74 (brd s, 1, CH), 7.05 (s, 3, SCH_3), 7.6–9.0 (m, 10, ring 5 CH_2).

A mixture of *N*-(1.4-dimethylcyclohexyl)methansulfonamide stereoisomers (*cis*-**4** and *trans*-**4**) was prepared by mesylation of a 1,4-dimethylcyclohexylamine (cis–trans mixture), which had been prepared in a way similar to the preparation of 1-methylcyclohexylamine.[21] The sulfonamides were well separated into the cis and the trans isomers using column B. The assignment of each stereoisomer was assigned in comparison with the products obtained from the stereospecific insertions of singlet methanesulfonylnitrene into the tertiary C–H bonds of *cis*- and *trans*-1,4-dimethycyclohexanes.[12,13]

N-(*trans*-1,4-Dimethylcyclohexyl)methanesulfonamide (*trans*-**4**): IR (neat) 3295 (NH), 1323 and 1153 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 5.44 (brd, s, 1 NH), 7.00 (s, 3, SCH_3), 8.57 (s, 3, CH_3), 9.07 (d, 3, CH_3), 7.67–9.57 (m, 9, ring CH and 4 CH_2).

Anal. Calcd for $C_9H_{19}O_2NS$: C, 52.65; H, 9.32; N, 6.82. Found: C, 52.48; H, 9.29; N, 6.85.

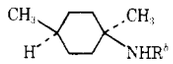
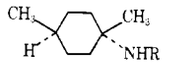
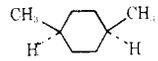
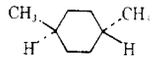
N-(*cis*-1,4-Dimethylcyclohexyl)methanesulfonamide (*cis*-**4**): IR (neat) 3285 (NH), 1325 and 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 5.35 (brd s, 1, NH), 6.97 (s, 3, SCH_3), 8.58 (s, 3, CH_3), 9.08 (d, 3, CH_3), 7.90–9.58 (m, 9, ring CH and 4 CH_2).

Anal. Found: C, 52.46; H, 9.33; N, 6.86.

Sensitized Photolyses of 1 in Hydrocarbons. A solution of 1.50 g (0.0124 mol) of methanesulfonyl azide (**1**) and 1.78 g (0.015 mol) of acetophenone in a mixture of hydrocarbon (0.15 mol) and 1,2-dichloroethane (0.3 mol) was stirred at 25 °C and irradiated by a high-pressure mercury lamp until the evolution of nitrogen was no longer observed. The nitrogen was produced in almost the theoretical amount, based on the azide used. The excess substrate was removed by distillation at 50–80 °C under 20–30 mmHg pressure. The residue was analyzed by VPC on columns B and C. Methanesulfonamide (**5**) had IR and NMR spectra and a VPC retention time identical with those of the authentic sample.

A. In Cyclohexane: *N*-Cyclohexylmethanesulfonamide (**4A**, 0.39 g) and bicyclohexyl (0.8 g) were isolated. Bicyclohexyl and **4A** had IR and NMR spectra and VPC retention times identical with those of authentic samples.

Table III. Reaction of 1 with *cis*- and *trans*-1,4-Dimethylcyclohexanes

Hydrocarbon (3)	Product,[a] %			
	 *trans*-4	 *cis*-4	*cis*-8 or *trans*-8	RNH_2 (5)
 *cis*-3	13.8 (0)[c]	4.3 (3.3)	8.7 (5.8)	21.9 (49.0)
 *trans*-3	12.9 (3.6)	2.8 (0)	4.0 (5.0)	21.2 (35.0)

[a] Calculated on the basis of the azide used. [b] R = SO_2CH_3. [c] Parentheses indicate the values from direct photolyses.

B. In 2-Methylbutane: *N*-(1,1-Dimethylpropyl)methanesulfonamide (**4B$_1$**, 0.24 g) and *N*-(1,2-dimethylpropyl)methanesulfonamide (**4B$_2$**, 0.027 g) were isolated, **4B$_1$**: IR (neat) 3320 (NH), 1325 and 1150 cm^{-1} (SO_2); NMR (CCl_4) τ 5.10 (brd s, 1, NH), 7.10 (s, 3, SCH_3), 8.38 (q, 2, CH_2), 8.70 (s, 6, 2 CH_3), 9.08 (t, 3, CH_3).

Anal. Calcd for $C_6H_{15}O_2NS$: C, 43.60; H, 9.15; N, 8.47. Found: C, 43.48; H, 9.20; N, 8.42.

4B$_2$: IR (neat) 3300 (NH), 1320 and 1140 cm^{-1} (SO_2); NMR (CCl_4) τ 4.94 (brd s, 1, NH), 6.30–7.00 (m, 1, NCH), 7.10 (s, 3, SCH_3), 8.05–8.60 (m, 1, CH), 8.80 (d, 3, CH_3), 9.03 (d, 6, $2CH_3$).

Anal. Found: C, 43.71; H, 9.10; N, 8.40.

C. In 2,3-Dimethylbutane: *N*-(1,1,2-Trimethylpropyl)methanesulfonamide (**4C**, 0.27 g) was isolated: IR (neat) 3310 (NH), 1315 and 1145 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 5.59 (brd s, 1, NH), 6.98 (s, 3, SCH_3), 7.66–8.40 (m, 1, CH), 8.67 (s, 6, 2 CH_3), 9.07 (d, 6, 2 CH_3).

Anal. Calcd for $C_7H_{17}O_2NS$: C, 46.89; H, 9.55; N, 7.81. Found: C, 46.86; H, 9.50; N, 7.68.

D. In *cis*-3: *trans*-**4** (0.35 g), *cis*-**4** (0.11 g), and *N*-(*cis*-2,5-dimethylcyclohexyl)methanesulfonamide (*cis*-**8**, 0.22 g) were isolated. *cis*-**8**: IR (neat) 3250 (NH), 1320 and 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 5.48 (brd s, 1, NH), 7.20 (s, 3, SCH_3), 8.96 (d, 3, CH_3), 9.08 (d, 3, CH_3), 7.80–9.27 (m, 9, ring 3 H and 3 CH_2).

Anal. Calcd for $C_9H_{19}O_2NS$: C, 52,65; H, 9.32; N, 6.82. Found: C, 52.43; H, 9.27; N, 6.78.

E. In *trans*-3: *trans*-**4** (0.33 g), *cis*-**4** (0.07 g), and *N*-(*trans*-2,5-dimethylcyclohexyl)methanesulfonamide (*trans*-**8**, 0.1 g) were isolated. *trans*-**8**: IR (neat) 3270 (NH), 1320 and 1145 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 5.50 (brd s, 1, NH), 7.06 (s, 3, SCH_3), 8.98 (d, 3, CH_3), 9.18 (d, 3, CH_3), 7.70–9.30 (m, 9, ring 3 CH and 3 CH_2).

Anal. Found: C, 52.51; H, 9.30; N, 6.80.

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Registry No.—1, 1516-70-7; cyclohexane, 110-82-7; 2-methylbutane, 78-78-4; 2,3-dimethylbutane, 79-29-8; **4A**, 19299-40-2; **4B$_1$**, 39653-34-4; **4C**, 64235-77-4; **4B$_2$**, 39653-33-3; *cis*-**3**, 624-29-3; *trans*-**3**, 2207-04-7; *trans*-**4**, 64235-76-3; *cis*-**4**, 64235-75-2; **8**, 64235-80-9; cyclohexylamine, 108-91-8; methanosulfonzl chloride, 124-63-0; *cis*-1,4-dimethylcyclohexylamine, 64235-79-6; *trans*-1,4-dimethylcyclohexylamine, 64235-78-5.

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