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INSERTION OF METHANESULFONYLNITRENE INTO C-H AND O-H BONDS

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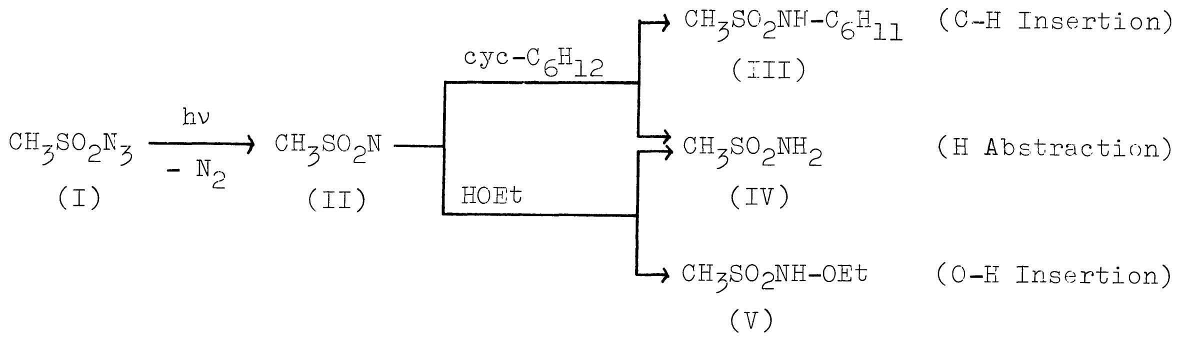
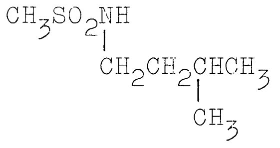
The insertion of methanesulfonylnitrene into C-H and O-H bonds was investigated by the photolysis of methanesulfonyl azide in hydrocarbons and in alcohols. The relative reactivity of the sulfonylnitrene toward C-H bonds of hydrocarbons was found to be smaller than that of ethoxycarbonylnitrene, whereas the reactivity of the sulfonylnitrene toward O-H bonds of alcohols was larger than that of the carbonylnitrene.

The relative reactivities of nitrenes toward primary, secondary, and tertiary C-H bonds have been reported for phenylnitrene,[1] cyanonitrene,[2] and carbonylnitrenes.[3~7] In regard to sulfonylnitrene, however, satisfactory results have not been obtained in the thermal decomposition of *p*-toluenesulfonyl azide in 2-methylbutane.[8] We employed methanesulfonyl azide as a precursor of sulfonylnitrene, and could determine the relative reactivities of the nitrene toward C-H and O-H bonds.

Irradiation of methanesulfonyl azide (I, 25 mmole) in a mixture of cyclohexane (0.5 mole) and dichloromethane (0.5 mole), with the light of a low pressure mercury lamp at 0 °C, gave *N*-cyclohexylmethanesulfonamide (III, 18.3 %) and methanesulfonamide (IV, 38.4 %). Irradiation of I (25 mmole) in ethanol (1 mole) gave *N*-ethoxymethanesulfonamide (V, 48.8 %) and IV (43.3 %), accompanied by acetaldehyde which was identified as the 2,4-dinitrophenylhydrazone. The formation of III, IV, and V suggests that the reaction involves methanesulfonylnitrene (II) as an intermediate.[9]

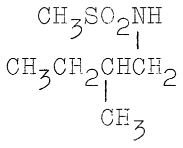


Irradiation of I (10 mmole) in a dichloromethane (0.5 mole) solution of 2-methylbutane (0.5 mole) yielded a mixture of four insertion products of II into the C-H bonds of 2-methylbutane, VIa∼VId, besides a hydrogen abstraction product (IV, 45 %). The isomers of VI were identified by their IR and NMR spectra, and their elemental analyses. The isomer VIa (found in the lowest yield) was also identified by comparison with an authentic sample. In Table 1, the relative reactivities (corrected for the number of hydrogen of each type) of methanesulfonylnitrene towards the primary, secondary, and tertiary C-H bonds in 2-methylbutane were compared with those of other carbonylnitrenes.


$CH_3SO_2NHCH_2CH_2CH(CH_3)CH_3$

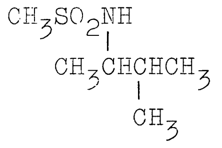
(VIa)

1.04 %


$CH_3CH_2CH(CH_3)CH_2NHSO_2CH_3$

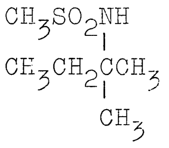
(VIb)

2.31 %


$CH_3CH(NHSO_2CH_3)CH(CH_3)CH_3$

(VIc)

3.11 %


$CH_3CH_2C(CH_3)_2NHSO_2CH_3$

(VId)

3.58 %

Table 1. Relative Reactivities of Nitrenes toward the C-H Bonds of 2-Methylbutane (per C-H Bond)

Nitrene	CH_3 ↑	CH_2 ↑	$CH(CH_3)_2$ ↑
CH_3SO_2-N*	1	4.2(± 5 %)**	9.6(± 3 %)
EtOCO-N[4]	1	9 (±10 %)	34 (± 5 %)
EtOCOCC-N[7]	1	6.6(±10 %)	44 (±13 %)
Me_3CCO-N[6]	1	8.9(±10 %)	160 (±25 %)

*The values for methanesulfonylnitrene were obtained by vapor phase chromatographical determination of the isomers of VI using benzamide as an internal standard.[10]

**The relative errors appear in parentheses.

The results indicate that the sulfonylnitrene seems to be less selective than carbonylnitrenes. Carbonylnitrenes could be stabilized by a resonance between monovalent nitrogen atom and carbonyl groups, whereas the sulfonylnitrene has no resonance forms other than those involving d-orbital expansion on the sulfur atom.

In order to compare the reactivities of C-H bonds of 2-methylbutane with those of cyclohexane, the photolysis of I (5 mmole) was carried out in an equimolar solution of 2-methylbutane (0.25 mole) and cyclohexane (0.25 mole) in dichloromethane (0.5 mole). The results are summarized in Table 2. The relative reactivity toward primary, secondary, and tertiary C-H bonds was found in satisfactory agreement with that obtained in 2-methylbutane (Table 1).

Table 2. Relative Reactivity of Methanesulfonylnitrene toward the C-H Bonds of 2-Methylbutane and Cyclohexane

Product	VIa	VIb	VIc	VId	III	IV
Yield, mole %	0.70	1.42	2.30	2.06	14.2	43
Type of C-H bond	1°		2°	3°	cyc C-H	
Relative reactivity	1		4.7(±2 %)	8.7(±4 %)	5.0(±6 %)	

In the next place, comparison of the reactivity of I toward C-H bond with that toward O-H bond was attempted. The photolysis of I (25 mmole) in a mixture of ethanol (0.25 mole) and cyclohexane (0.25 mole) gave V and III in the yields of 35 % and 14 %, respectively. From these data, the relative reactivity of O-H bond per cyclic C-H bond was calculated to be 29. This value was combined with that of relative reactivity shown in Table 2. The results are listed in Table 3.

Table 3. Relative Reactivities of Nitrenes toward C-H Bonds and O-H Bond

Nitrene	CH_3 ——	CH_2 ——	$CH(CH_3)_2$	cyc-C_6H_{12}	C_2H_5O-H
CH_3SO_2-N	0.2	0.95	1.8	1	29
EtOCO-N[11]	0.09	0.8	3.0	1	23

Compared methanesulfonylnitrene with ethoxycarbonylnitrene, the former is more *reactive* reagent than the latter in the insertion into O-H bond, in spite of that the former is less *selective* reagent than the latter in the insertion into C-H bonds. It is assumed that an electrophilicity of nitrene become a dominant factor in the insertion reaction toward O-H bond. The reaction of sulfonylnitrene toward an O-H bond, therefore, proceeds by the O-N ylide mechanism[12)] in analogy with the case of carbonylnitrene.

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