CHEMISTRY LETTERS, pp. 1243-1246, 1973. Published by the Chemical Society of Japan

α-ELIMINATION OF N,N-DICHLOROMETHANESULFONAMIDE IN THE PRESENCE OF COPPER

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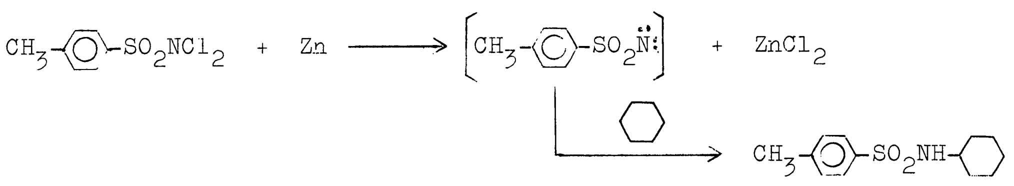
It was found that N,N-dichloromethanesulfonamide (I) reacted with cyclic ethers and hydrocarbons in the presence of copper to give the N-substituted methanesulfonamides (II) and methanesulfonamide. The non-stereospecific formation of II in the reaction of I with trans- and cis-1,4-dimethylcyclohexanes, contrary to the stereospecific formation of II in the reaction of methanesulfonyl azide with the hydrocarbons, gives a support to a radical mechanism.

It has been reported that refluxing a cyclohexane solution of dichloramine-T in the presence of zinc dust gives N-cyclohexyl-p-toluenesulfonamide in poor yield (6 %).[1) On stirring chloramine-T with copper powder in dioxane at 25 °C, p-tolylsulfonamidodioxane was formed in a 70 % yield.[2) For the formation of these products, a nitrene intermediate was postulated. This intermediacy aroused an interest in our study of sulfonylnitrenes.[3) The present letter reports the decomposition of N,N-dichloromethanesulfonamide in the presence of copper powder, the results being compared with those of the decomposition of methanesulfonyl azide.



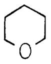
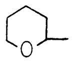
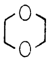
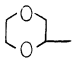
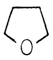
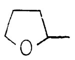
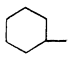
Copper powder (0.075 mol) was suspended in a substrate, ethers or hydrocarbons (0.6 mol), and N,N-dichloromethanesulfonamide (I, 0.025 mol) in small portions was added to the suspension in a stream of nitrogen with stirring. The reaction with the ethers was carried out at 5—7 °C except with dioxane at 12 °C. The reaction with the hydrocarbons was carried out at 70 °C. The reaction gave the N-substituted methanesulfonamides (II) and methanesulfonamide (III) (Table 1).

$$\underset{\text{(I)}}{CH_3SO_2NCl_2} + R'H \xrightarrow{Cu} \underset{\text{(II)}}{CH_3SO_2NHR'} + \underset{\text{(III)}}{CH_3SO_2NH_2}$$

(R' : ether rest or hydrocarbon rest)

The products, II and III, correspond formally to those from insertion into the C-H bonds and from abstraction of the hydrogen atoms, respectively, by methanesulfonylnitrene. In the reactions with tetrahydropyran and tetrahydrofuran (THF),

Table 1. Reaction of I with Cyclic Ethers and Cyclohexane

Substrate	Product (%)[a]		
	II[b]		III
	 NHR	52	41
	 NHR	46	48
	 NHR	46	45
	 NHR	5.4	60

a) The yields were calculated based on the amount of I used.

b) R : CH_3SO_2

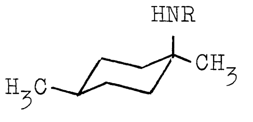
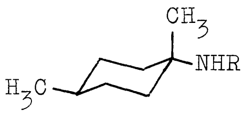
no derivatives of the substrates were obtained other than the α-substituted derivatives.[4]

Thermal (130 °C) or photochemical (mainly 2537 Å) decomposition of methanesulfonyl azide (IV) in a dichloromethane solution of trans-1,4-dimethylcyclohexane (trans-V) gave the insertion product (trans-II) of methanesulfonylnitrene[3] into the tertiary C-H bond besides III. In the same manner, the reaction of IV with cis-1,4-dimethylcyclohexane (cis-V) gave the insertion product (cis-II) into the tertiary C-H bond (Table 2). Neither the formation of trans-II from cis-V nor that of cis-II from trans-V was observed gas chromatographically. This stereospecific formation of II indicates that only the singlet sulfonylnitrene inserts into the C-H bond but the triplet nitrene does not.[5]

Contrary to the reaction of IV, the reaction of I with trans-V or cis-V in the presence of copper powder gave a 1 : 1 mixture of trans-II and cis-II along with III (Table 2). The non-stereospecific formation of II in the reaction of I means that neither the singlet nitrene nor the triplet nitrene takes part in the production of II, because the triplet nitrene can not insert into C-H bond as described above.

The reaction of I in 2-methylbutane in the presence of copper powder gave one product (VI) with the tertiary C-H bond, in comparison with that the reaction of IV gave four isomeric insertion products into all of the primary, secondary, and tertiary C-H bonds (Table 3). Also from the difference of the selectivities toward such C-H bonds,[6] a nitrene mechanism may be ruled out for the formation of II and VI.

Table 2. Reaction of I or IV with trans- and cis-1,4-Dimethylcyclohexanes a)

I or IV		V	Yield of product (%) b)		
			 (trans-II)	 (cis-II)	III
$RNCl_2$ c)		trans	12.4	11.0	61
		cis	12.1	10.3	60
RN_3 d)	Δ	trans	4.0	0	9.8
		cis	0	3.2	8.5
	hν	trans	3.6	0	35
		cis	0	3.3	49

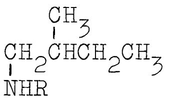
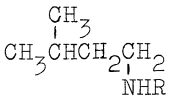
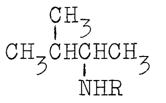
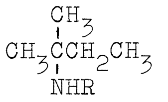
a) R : CH_3SO_2

b) Calculated based on the amounts of I and IV used.

c) Trace amounts of the isomeric secondary substituted derivatives of V were detected gas chromatographically in the both reactions with trans-V and cis-V.

d) The thermolyses gave the isomeric insertion products into the secondary C-H bonds of V in a 5.8 % yield besides trans-II and in a 5.7 % yield besides cis-II respectively. The photolyses gave those in a 5.0 % yield besides trans-II and in a 5.8 % yield besides cis-II respectively.

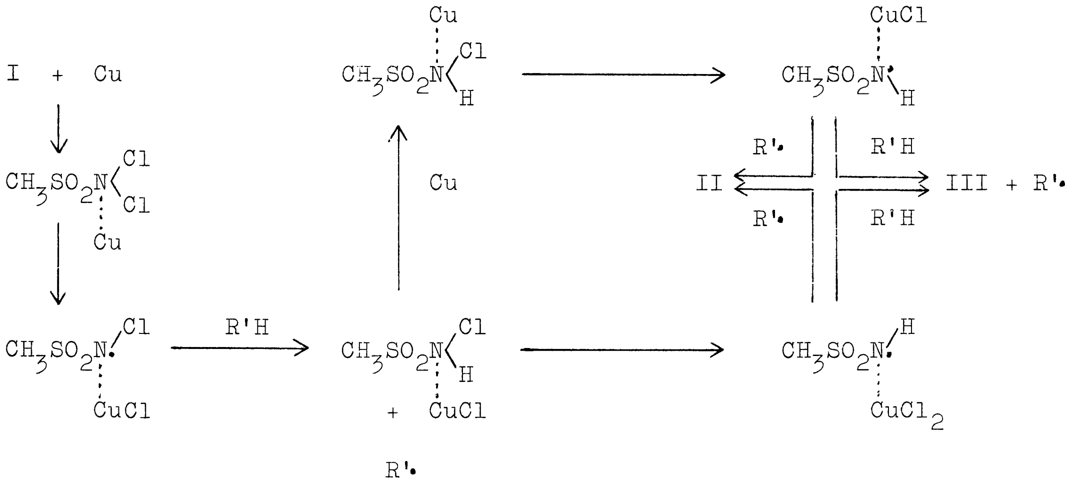
Table 3. Reaction of 2-Methylbutane

I or IV	Yield of product a) (%) b)				
	 $CH_2(NHR)CH(CH_3)CH_2CH_3$	 $CH_3CH(CH_3)CH_2CH_2NHR$	 $CH_3CH(CH_3)CH(NHR)CH_3$	 $CH_3C(CH_3)(NHR)CH_2CH_3$	RNH_2
$CH_3SO_2NCl_2$	ND c)	ND	ND	6.9	62.9
$CH_3SO_2N_3$ d)	2.31	1.04	3.11	3.58	45.0

a) R : CH_3SO_2 b) Calculated based on the amounts of I and IV used.

c) ND : Not detected. d) The photolysis values from Ref. 3.

The reaction of I described above was repeated in the presence of hydroquinone as a potential radical inhibitor. Thus, when V was employed, the addition of 0.06 mol of hydroquinone reduced the yield of II from 23 % to below 0.3 %, while increasing the yield of III from 60 % to 77 %. In the case of employing THF, II was not detected, while the yield of III increased from 45.6 % to 98.4 %.[7] This fact suggests that the reaction of I with the substrates in the presence of copper powder proceeds involving a radical mechanism. A tentative reaction mechanism, which perhaps involvs a metal-radical-complex, may be outlined in a following scheme.



The reaction of I with the above substrates gave the same products also in the presence of cuprous chloride instead of copper. The reaction with THF, thus, gave II and III in a yield of 57.6 % and 42.3 %, respectively, and the reaction with trans-V gave trans-II, cis-IT, and III in a yield of 9.7 %, 7.3 %, and 59.4 %, respectively. Details of these reactions and the reaction mechanism will be discussed in later papers.

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4) T. Shingaki, M. Inagaki, N. Torimoto, and M. Takebayashi, ibid., 1972, 297.
5) T. Shingaki, M. Inagaki, N. Torimoto, and M. Takebayashi, ibid., 1972, 155.
6) Despite different reaction conditions (thermolysis, photolysis, and α-elimination), the relative reactivities of ethoxycarbonylnitrene toward the various sites on 2-methylbutane differ only slightly; W. Lwowski, Angew. Chem., 79, 922 (1967); ibid., Int. Ed. Engl., 6, 897 (1967); W. Lwowski, "Carbonylnitrenes", in "Nitrenes", Ed. by W. Lwowski, Interscience Publishers, New York (1970), p.201; see Ref. 5.
7) The presence of hydroquinone during the thermal decomposition of ethyl azidoformate in cyclohexane raised the yield of cyclohexylurethan (insertion by the singlet nitrene), while decreasing the yield of urethan (abstraction by the triplet nitrene); D.S. Breslow and E.I. Edwards, Tetrahedron Lett., 1967, 2123.

(Received September 29, 1973)