Copper-initiated Decomposition of *N*,*N*-Dichloromethanesulfonamide

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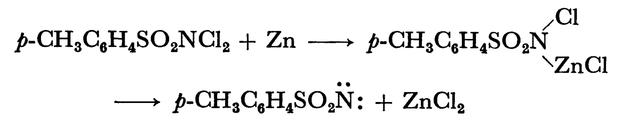
The reactions of *N*,*N*-dichloromethanesulfonamide (I) with substrates such as hydrocarbons and ethers gave the *N*-substituted methanesulfonamide (II) and methanesulfonamide (III) in the presence of copper. The reaction with 2-methylbutane gave the product only with a tertiary C–H bond, though the singlet nitrene which was generated from methanesulfonyl azide reacted with the primary, secondary, and tertiary C–H bonds in the ratio of 1: 4.2: 9.6. The reactions with the tertiary C–H bonds of *cis*- and *trans*-1,4-dimethylcyclohexanes proceeded non-stereospecifically, in contrast to those of the nitrene with them. The addition of a radical inhibitor, hydroquinone, reduced the yield of II, while it increased the yield of III. The reaction with alcohols led to a quantitative yield of III, accompanied by the corresponding aldehydes. These results suggest that the reaction proceeds not by a nitrene mechanism, but by a metal-radical mechanism.

The existence of a nitrene intermediate has been shown in several reactions which afford the same products or product mixtures *via* two or more independent routes. Phenylnitrene, for example, seems to be the intermediate in the pyrolysis[1] and photolysis[2] of phenyl azide, in the deoxygenation of nitrosobenzene[3] and nitrobenzene,[4] and in the photolyses of oxaziridines,[5] for the intermediate always leads to the same product, 2-dialkylamino-3*H*-azepine, in the presence of a dialkylamine. The species generated by the photolysis[6] and the thermolysis[7] of ethyl azidoformate and by the α-elimination of *N*-(*p*-nitrophenylsulfonyloxy)urethane[8] nearly the same regioselectivities toward the C–H bonds of 2-methylbutane. These demonstrations have been explained by the intervention of ethoxycarbonylnitrene in each instance.

Breslow and Sloan[9] reported that the reaction of dichloramine-T with zinc dust in cyclohexane gave *N*-cyclohexyl-*p*-toluenesulfonamide, and suggested that a free sulfonylnitrene was formed as an intermediate, since the insertion into C–H bonds is a distinctive nitrene reaction:



$$p\text{-}CH_3C_6H_4SO_2NCl_2 + Zn \longrightarrow p\text{-}CH_3C_6H_4SO_2N\begin{matrix}\diagup Cl\\ \diagdown ZnCl\end{matrix}$$

$$\longrightarrow p\text{-}CH_3C_6H_4SO_2\ddot{N}: + ZnCl_2$$

(sulfonylnitrene)

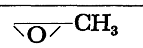
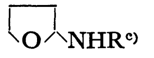
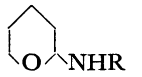
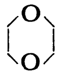
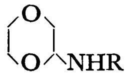
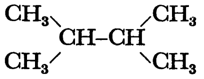
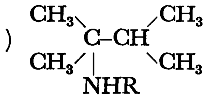
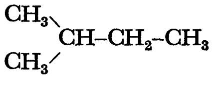
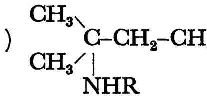
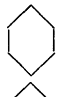
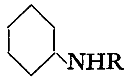
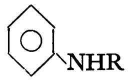
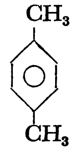
On the other hand, the thermolysis of *N*,*N*-dichloromethanesulfonamide in benzene afforded methanesulfonamide in an 82% yield, with gas-chlomatographically detectable biphenyl, but neither *N*-mesylaniline nor azepine derivatives.[10] This finding, by Abramovitch, shows that the formation of nitrene in the reaction might be ruled out. Prior to his paper, we ourselves reported that the reaction of *N*,*N*-dichloromethanesulfonamide (I) with hydrocarbons and ethers in the presence of copper proceeded by means of a radical mechanism involving no sulfonylnitrene.[11]

We are investigating decomposition mechanisms of chloramide. As a part of this work, the reactions of I with the substrate hydrocarbons, ethers, and alcohols have been studied in further detail. The results will be discussed here in comparizon with those of the direct and the sensitized photolyses of methanesulfonyl azide.

Results and Discussion

Reactions of I in the Presence of Copper. Copper powder was suspended in a substrate (IV), and *N*,*N*-dichloromethanesulfonylamide (I) was added to the stirred suspension in small portions in a stream of nitrogen. The yields of the products are listed in Table 1.

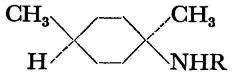
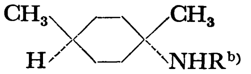
TABLE 1. REACTION OF I WITH ETHERS AND HYDROCARBONS

	Substrate (IV)		Product (%)[a] II		III
(a)		(a)	ND[b]		42
(b)		(b)		46	46
(c)		(c)		52	41
(d)		(d)		46	48
(e)		(e)		7.0	63
(f)		(f)		7.0	65
(g)		(g)		5.4	60
(h)		(h)		5.6	62
(i)		(i)		9.1	53

a) Calculated on the basis of the I used. b) ND: not detected. c) R: SO_2CH_3.

Each of the reactions gave the *N*-substituted methanesulfonamide (II) and methanesulfonamide (III).

TABLE 2. REACTION OF I WITH *cis*- AND *trans*-1,4-DIMETHYLCYCLOHEXANES

I or V		IV	Product (%)[a)]		
			 (*trans*-II)	 (*cis*-II)	III
$RNCl_2$		*trans*	12.4	11.0	61
		cis	12.1	10.3	60
RN_3	direct	*trans*	3.6	0	35
		cis	0	3.3	49
	sensitized	*trans*	12.9	2.8	22
		cis	13.8	4.3	22

a) Calculated on the basis of the I and V used. b) R: SO_2CH_3.

$$CH_3SO_2NCl_2 + R'\text{-}H \xrightarrow{Cu} CH_3SO_2NHR' + CH_3SO_2NH_2$$

(I) (II) (III)

(R′: hydrocarbon rest or ether rest)

The products, II and III, correspond formally to those from insertion into the C–H bonds, and from the abstraction of the hydrogen atoms, by methylsulfonylnitrene respectively. In the reactions with cyclic ethers, the α-substituted derivatives were isolated in good yields. The preferential formation of the α-substituted derivatives in IVb and IVc parallel those in the direct and sensitized photolyses of ethyl azidoformate in cyclic[13)] and acyclic[12)] ethers. The reaction of I with propylene oxide gave large quantities of a colorless, viscous substance whose IR spectrum showed a strong O–H stretching absorption. The products with the ring or the methyl C–H bonds were not isolated. The reactions in IVe and IVf gave, besides III, products with only the tertiary C–H bonds. This finding for the reaction with IVf is different from that of the direct photolysis of methanesulfonyl azide (V) in IVf; the singlet sulfonylnitrene generated by the direct photolysis reacted with the primary, secondary, and tertiary C–H bonds of IVf in the ratio of 1: 4.2: 9.6.[14)] The difference in the regioselectivities toward the C–H bonds between the present reaction and the photolysis of V means that the singlet sulfonylnitrene is probably not involved in the former.

Attempting the reaction of I with aromatic substrates, the decomposition in *p*-xylene gave the reaction product (IIi) with only the side-chain C-H bond, although the reaction in benzene gave that with the aromatic nucleus, besides III. On the contrary, the thermolysis of V in toluene gave no *N*-benzylmethanesulfonamide corresponding to IIi, but methanesulfonyltoluidide isomers and III in 76.8 and 22.7% yields respectively.[15)] Such aromatic nucleus derivatives are formed *via* an aziridine intermediate or a transition state with the sulfonylnitrene.[15,16)] The formation of IIi in the present reaction also supports the idea that the reaction proceeds by means of a mechanism involving no singlet nitrene.

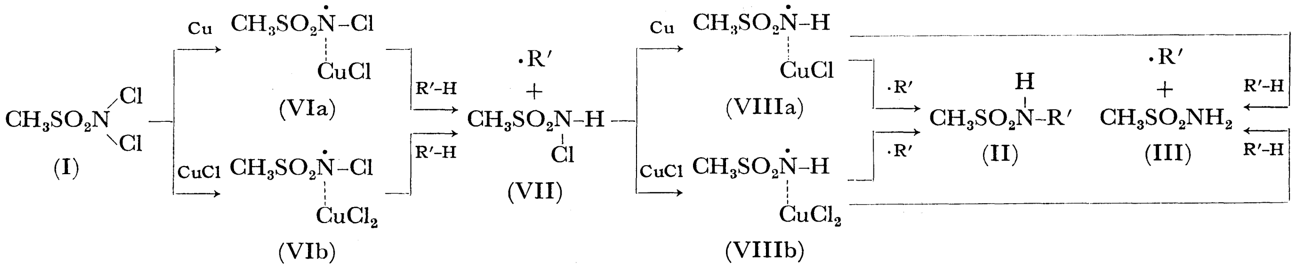
Next, the reactions of I were carried out in *cis*- and *trans*-1,4-dimethylcyclohexanes (*cis*-IV and *trans*-IV) in order to obtain information about the stereospecificity. The results are listed in Table 2, where they are compared with those of the direct[11)] and the sensitized[17)] photolyses of V. The reaction of I with either *cis*-IV or *trans*-IV gave a mixture of *cis*-II and *trans*-II (stereoisomers). On the other hand, in the photolyses of V, only one product isomer (*cis*-II or *trans*-II) was isolated in each reaction; the reaction was virtually completely stereospecific. The insertion of the sulfonylnitrene into the C–H bonds of hydrocarbons is a concerted reaction involving the singlet nitrene. Breslow *et al.* also recently reported that the insertion of methylsulfonylnitrene, generated by the thermolyses of V, into the tertiary C–H bonds of *cis*- and *trans*-1,2-dimethylcyclohexanes proceeded stereospecifically.[18)] The stereospecific formation of *cis*-II or *trans*-II shows that the radical, $CH_3SO_2\dot{N}H$, produced by the hydrogen abstraction of the triplet nitrene is not able to recombine with a hydrocarbon radical. Therefore, the non-stereospecific formation of *cis*-II or *trans*-II in the reactions of I means that neither the singlet nor the triplet nitrene takes part in the formation of II. The non-stereospecific formation of *cis*-II or *trans*-II in the sensitized photolyses of V can be explained by the triplet azide mechanism.[17)]

The reactions of I with ethyl alcohol and butyl alcohol did not give the product with the O–H bonds, but the hydrogen abstraction product, III, in yields of 97.2 and 97.8% respectively, accompanied by the corresponding aldehydes. The formation of the aldehydes in the alcohols suggests that the reaction of I involves a radical process. Therefore, the reaction of I was repeated in the presence of hydroquinone as a potential inhibitor. When *cis*-IV was employed, the addition of the hydroquinone reduced the yield of the mixture of *cis*-II and *trans*-II from 23% to below 0.3%, while it increased the yield of III from 60 to 77%. When

TABLE 3. REACTION OF I IN THE PRESENCE OF COPPER (I) CHLORIDE

Substrate (IV)	Product (%)[a)]				
	II				III
IVb	IIb	57.6			43
trans-IV[b)]	*trans*-II	9.7	*cis*-II	7.3	60
cis-IV[b)]	*trans*-II	8.6	*cis*-II	6.1	64

a) Calculated on the basis of the I used. b) A mixture of IV and 1,2-dichloroethane in a molar ratio of 0.7: 0.3 was used.



R′: hydrocarbon rest or ether rest

Scheme 1.

IVb was employed, IIb was not detected, while the yield of III increased from 45.6 to 98.4%. These facts show that the reaction of I with the substrates in the presence of copper powder involves a radical mechanism.

Reactions of I in the Presence of Copper(I) Chloride. The reactions of I with the substrates were carried out in the presence of copper(I) chloride instead of copper. The yields of the products are listed in Table 3. The same products as those formed in the presence of copper were obtained. In the reaction with *cis*-IV and *trans*-IV, the products, II, were obtained only when 1,2-dichloroethane was used as a diluent, and the reactions were non-stereospecific.

Reaction Mechanism. A tentative reaction mechanism, which perhaps involves a metal-radical complex, may be outlined as in Scheme 1.

The reactions of I with the substrates do not proceed in the absence of copper or copper(I) chloride under our conditions. The decomposition of I must be initiated by copper or copper(I) chloride. The elimination of one chlorine atom gives a metal-radical complex (VI), followed by the formation of *N*-chloromethanesulfonamide (VII). The sulfonamide radical (VIII) which is formed from VII with copper or copper(I) chloride recombines with the substrate radical (·R′), giving II. On the other hand, VIII abstracts a hydrogen atom from the substrate to give III. It is well known that the metal-radical complex, generated from organic halides and transition metal compounds, behaves somewhat differently from those of radicals generated from such initiators as organic peroxides.[19] As has been mentioned above, the $CH_3SO_2\dot{N}H$ radical generated from V in hydrocarbons, was not able to recombine with a hydrocarbon radical. However, the radical generated by the present reaction would be stabilized by forming the metal-radical complex, as is shown in the Scheme. Consequently, the recombination of the radical with a hydrocarbon radical may be possible.

Photolyses of V in the Presence of Copper(I) Chloride. The presence of a metal compound in the photolysis of V would lead us to expect the recombination of $CH_3SO_2\dot{N}H$ with a hydrocarbon radical. Thus, the direct photolysis of V was carried out in *cis*-IV in the presence of copper(I) chloride. Unexpectedly, the reaction gave only one tertiary isomer, *cis*-II; the reaction was completely stereospecific. The sensitized photolyses of V were carried out in *cis*-IV and *trans*-IV in the presence of copper(I) chloride. As the photolyses proceeded, the solution had a color varying from an initial light yellow to dark green at the end. However, there was no significant difference in the product yields between the absence of copper(I) chloride (shown in Table 2) and its presence (shown in Table 4).

Table 4. Sensitized photolyses of V in the presence of copper(I) chloride

Hydrocarbon (IV)	Product (%)[a]		
	trans-II	*cis*-II	III
trans-IV	5.9	2.4	22
cis-IV	12.7	4.3	27

a) Calculated on the basis of of the I used.

The copper compound did not exhibit any effect on the reaction involving the azide, though it was evident that the copper compound played an important role in the present chloramide system; the absence of copper compound did not result in the formation of the *N*-substituted methanesulfonamide.[10]

Experimental

The IR spectra were recorded on a Hitachi EP-S photometer and a Nippon Bunko (JASCO) Model A-3 photometer, while the NMR spectra were taken on Hitachi R-20 and Hitachi R-24 instruments, using tetramethylsilane as the internal standard. The gas chromatography (VPC) was conducted on Shimadzu GC-2C and Nippon Denshi (JEOL) JGC 20K units by means of the following columns: A, 20% Ucon Oil 5 HB 2000 on Celite (60—80 mesh); B, 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 testing for the stability of each product during VPC analysis have been described in a previous paper.[20]

Materials. The *N*,*N*-dichloromethanesulfonamide (I) was prepared by the method of Newcombe.[21] The methanesulfonyl azide (V) was prepared by the method of Reagan and Nickon.[22] The propylene oxide, tetrahydrofuran, tetrahydropyran, 1,4-dioxane, 2,3-dimethylbutane, 2-methylbutane, cyclohexane, benzene, *p*-xylene, ethyl alcohol, butyl alcohol, and 1,2-dichloroethane were used after the commercial reagents had been purified according to the published directions.[23] Analytical-grade reagents of copper(I) chloride, copper, hydroquinone, and acetophenone were used without further purification. The preparation of *cis*- and *trans*-1,4-dimethylcyclohexanes (*cis*-IV and *trans*-IV) has already been described.[17]

Authentic Samples. The preparation of *N*-cyclohexylmethanesulfonamide (IIg), *N*-(*cis*-1,4-dimethylcyclohexyl)methanesulfonamide (*cis*-II), and *N*-(*trans*-1,4-dimethylcyclohexyl)-methanesulfonamide(*trans*-II) has been described previously.[17] *N*-Phenylsulfonamide (IIh) was prepared from aniline and methanesulfonyl chloride in a way similar to that used in the preparation of *N*-cyclohexylurethane;[24] mp 98 °C, IR (Nujol, cm^{-1}): 3270 (NH), 1330, and 1155 (SO_2). NMR ($CDCl_3$, τ): 2.70 (C_6H_5, 5H, s), 2.72 (NH, 1H, bs), and 7.00 (SCH_3, 3H, s).

Reactions of I with Ethers, Hydrocarbons, and Alcohols in the Presence of Copper. Copper powder (4.8 g, 0.075 mol) was suspended in a substrate (0.6 mol of ethers, hydrocarbons, or alcohols), and *N*,*N*-dichloromethanesulfonamide (I, 4.1 g, 0.025 mol) was added to the stirred suspension in small portions in a stream of nitrogen. The reactions with ethers and alcohols were carried out at 5—7 °C, except for that with dioxane, which was done at 12 °C. After I had been added, the stirring was continued for about another 5 h. Then the suspension was filtered, and the filtrate was concentrated under reduced pressure. In the reactions with hydrocarbons, the residue was analyzed by VPC on Column A and B. On the other hand, the residual material resulted from the filtration of the suspension was extracted with three 50-ml portions of 1M-hydrochloric acid and the hydrochloric acid was evaporated under reduced pressure. The abstraction product (III) contained in the residue was dissolved in ethyl alcohol and analyzed by means of VPC on Column A. In the cases of the ethers and alcohols, the residue was extracted with three 50-ml portions of hot benzene. The colorless crystals (II), obtained by evaporating the benzene, were dried *in vacuo* and weighed. The NMR spectrum of each of the crystals showed it to contain no contaminant. The crystals were then recrystalized from benzene, and the melting points were measured. On the other hand, III was also obtained from the insoluble material in the hot benzene. Methanesulfonamide (III), formed from every experiment, had IR and NMR spectra and a VPC retention time identical with those of the authentic sample.

In Tetrahydrofuran (IVb), Tetrahydropyran (IVc), and 1,4-Dioxane (IVd): *N*-(2-Tetrahydrofuryl)methanesulfonamide (IIb, 1.90 g), *N*-(2-tetrahydropyranyl)methanesulfonamide (IIc, 2.32 g), and *N*-(1,4-dioxan-2-yl)methanesulfonamide (IId, 2.08 g) were isolated respectively. IIb: Mp 75 °C, IR (Nujol, cm^{-1}): 3240 (NH), 1325, and 1170 (SO_2). NMR ($CDCl_3$, τ): 4.44 (NH, 1H, bs), 4.48—4.90 (ring-CH, 1H, m), 5.60—6.34 (ring δ-CH_2, 2H, m), 6.93 (SCH_3, 3H, s), and 7.33—8.52 (ring β- and γ-CH_2, 4H, m). Found: C, 36.10; H, 6.59; N, 8.30%. Calcd for $C_5H_{11}O_3NS$: C, 36.36; H, 6.71; N, 8.48%. IIc: Mp 102 °C, IR (Nujol, cm^{-1}): 3300 (NH), 1330, and 1155 (SO_2). NMR ($CDCl_3$, τ): 3.90 (NH, 1H, bd), 4.82—5.58 (ring-CH, 1H, m), 5.66—6.68 (ring ε-CH_2, 2H, m), 6.85 (SCH_3, 3H, s), and 7.78—8.74 (ring β-, γ- and δ-CH_2, 6H, m). Found: C, 39.81; H, 7.05; N, 7.75%. Calcd for $C_6H_{13}O_3NS$: C, 40.22; H, 7.31; N, 7.82%. IId: Mp 109 °C, IR (nujol, cm^{-1}): 3265 (NH), 1335, and 1155 (SO_2). NMR ($CDCl_3$, τ): 4.05 (NH, 1H, bd), 4.76—5.22 (ring-CH, 1H, m), 5.68—6.78 (ring-CH_2, 6H, m), and 6.90 (SCH_3, 3H, s). Found: C, 32.95; H, 6.01; N, 7.62%. Calcd for $C_5H_{11}O_4NS$: C, 33.14; H, 6.12; N, 7.73%.

In 2,3-Dimethylbutane (IVe), 2-Methylbutane (IVf), and Cyclohexane (IVg): *N*-(1,1,2-Trimethylpropyl)methanesulfonamide (IIe, 0.31 g), *N*-(1,1-dimethylpropyl)methanesulfonamide(IIf, 0.29 g), and *N*-cyclohexylmethanesulfonamide (IIg, 0.24 g) were isolated respectively. The IR and NMR spectra of IIe, IIf, and IIg have been described previously.[17]

In Benzene (IVh) and p-*Xylene (IVi)*: *N*-Phenylmethanesulfonamide (IIh, 0.24 g) and *N*-(*p*-tolylmethyl)methanesulfonamide (IIi, 0.45 g) were isolated. The IR and the NMR spectra of IIh were identical with those of the authentic sample. IIi: IR (neat, cm^{-1}): 3260 (NH), 1330, and 1160 (SO_2). NMR ($CDCl_3$, τ): 2.83 (C_6H_4, 4H, s), 5.00 (NH, 1H, bs), 5.75 (CH_2, 2H, d), 7.19 (SCH_3, 3H, s), and 7.66 (CH_3, 3H, s). Found: C, 53.81; H, 6.43; N, 6.92%. Calcd for $C_9H_{13}O_2NS$: C, 54.26; H, 6.58; N, 7.03%.

In trans-*IV*: *N*-(*trans*-1,4-Dimethylcyclohexyl)methanesulfonamide (*trans*-II, 0.63 g) and *N*-(*cis*-1,4-dimethylcyclohexyl)-methanesulfonamide (*cis*-II, 0.56 g) were isolated. The IR and the NMR spectra of *trans*-II and *cis*-II have been described previously.[17]

In cis-*IV*: *trans*-II (0.62 g) and *cis*-II (0.53 g) were isolated.

In Ethyl Alcohol and Butyl Alcohol: For each of the reactions with alcohols, the excess substrate and the volatile product, aldehyde, were trapped in a flask immersed in a dry ice-methanol bath reduced pressure. The trapped solution was added to a 2,4-dinitrophenylhydrazine solution, and the aldehyde was converted to the hydrazone. For ethyl alcohol and butyl alcohol, acetaldehyde and butyraldehyde were isolated as the hydrazones in yields of 2.30 g (41.1%) and 0.42 g (6.7%) respectively.

Reaction of I with IVb and cis-*IV in the Presence of Copper and Hydroquinone.* Hydroquinone (2.8 g, 0.025 mol) was added to the system of I-substrate-copper mentioned above. The reaction with IVb was carried out at 5—7 °C, while that with *cis*-IV was carried out at 70 °C. The reaction mixture was treated with the procedures described for the reaction in the absence of hydroquinone. In the reaction with *cis*-IV, trace amounts (0.01 g) of a mixture of *trans*-II and *cis*-II were isolated. In the reaction with IVb, only the abstraction product (III) was isolated.

Reaction of I with Ether and Hydrocarbons in the Presence of Copper(I) Chloride. Copper(I) chloride (7.1 g, 0.075 mol) was suspended in ether (0.5 mol) or a mixture of hydrocarbon (0.35 mol) and 1,2-dichloroethane (0.15 mol). I (4.1 g, 0.025 mol) in small portions was then added to the stirred suspension in a stream of nitrogen. The reaction with IVb was carried out at 5—7 °C, while those with *trans*-IV and *cis*-IV were carried out at 70 °C. After I had been added, the reaction mixture was treated with the procedures described for the reaction in the presence of copper.

In IVb: IIb (2.37 g) was isolated.

In trans-*IV*: *trans*-II (0.50 g) and *cis*-II (0.37 g) were isolated.

In cis-IV: *trans*-II (0.44 g) and *cis*-II (0.31 g) were isolated.

Sensitized Photolyses of Methanesulfonyl Azide (V) in Hydrocarbons in the Presence of Copper(I) Chloride. A powder of copper (I) chloride (1.9 g, 0.019 mol) was suspended in a mixture of V (1.5 g, 0.0124 mol), hydrocarbon (0.15 mol), 1,2-dichloroethane (0.3 mol), and acetophenone (0.15 mol). The mixture was then irradiated, with stirring at 25 °C, by a high-pressure mercury lamp under an atmosphere of nitrogen. A 1.5M-$CuSO_4$ aqueous solution was circulated as a filter. The filter completely inhibited the direct excitation of V. The irradiation was continued until the evolution of nitrogen was no longer observed. After the copper compound had been filtered out, the excess substrate was removed by distillation at 50—80 °C under 20—30 mmHg. The residue was analyzed by VPC on Columns A and B.

In trans-*IV*: *trans*-II (0.15 g) and *cis*-II (0.06 g) were isolated.

In cis-*IV*: *trans*-II (0.32 g) and *cis*-II (0.11 g) were isolated.

Direct Photolysis of V in cis-*IV in the Presence of Copper(I) Chloride.* A powder of copper(I) chloride (1.9 g, 0.019 mol) was suspended in a mixture of V (1.5 g, 0.0124 mol), *cis*-IV (0.15 mol), and 1,2-dichloroethane (0.3 mol). The suspension was irradiated, with stirring and cooling at 0 °C, by a low-pressure mercury lamp (mainly 2537 Å) under an atmosphere of nitrogen until the evolution of nitrogen was no longer observed. Then, the reaction mixture was treated with the procedures described for the sensitized photolyses. *cis*-II (0.12 g, 4%) was isolated.

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