SHORT COMMUNICATIONS

Photodecomposition of Azidoformate in Alkyl Sulfides. I

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The reaction of azidoformate in alkyl sulfides under photolytical conditions has received little attention. We wish to describe the formation of a stable iminosulfurane by photoinduced reaction of methyl azidoformate with alkyl sulfides, and some properties of singlet and triplet carbomethoxynitrene in alkyl sulfides.

Irradiation of a solution of 1 mmol methyl azidoformate in 10 mmol of alkyl sulfide was carried out in quartz vessels under nitrogen atmosphere with a high pressure mercury lamp for one hour. *N*-Methoxycarbonylalkyliminosulfuranes (I—III) were obtained as pale yellow liquids in 40—60% yields by passing the reaction mixture through a silica gel column using ethyl ether, then methanol-ethyl ether (1 : 4) as eluting solvents. The structures of the sulfuranes are determined by comparison of their spectra with those of authentic samples.[1]

Product patterns resulting in photosensitized reaction of azidoformate with sulfides are quite different from those in direct photolysis.

$$N_3CO_2CH_3 + R_2S \xrightarrow{h\nu} R_2\overset{\oplus}{S}—\overset{\ominus}{N}CO_2CH_3 \quad \text{40—60\% yields}$$

I, $R=CH_3$;
II, $R=C_2H_5$;
III, $R=i\text{-}C_3H_7$

A mixture of methyl azidoformate and alkyl sulfides (molar ratio 1 : 10) in Pyrex tubes was irradiated with a high pressure mercury lamp in the presence of acetophenone as triplet sensitizer.[2,3] Methyl carbamate was obtained as a major product (56% yield). Formation of alkyliminosulfuranes was not recognized from the NMR spectrum.

These results indicate that the triplet nitrene cannot be an intermediate of the formation of imonosulfuranes, analogous to the behaviors of carbene towards sulfur containing molecules.[4,5] This suggests a mechanism of iminosulfurane formation in which a singlet carbomethoxynitrene attacks an unshared electron pair on the sulfur atom of alkyl sulfides.

Table 1. Reaction of carbomethoxynitrene in a mixture of *cis*-4-methyl-2-pentene and dimethyl sulfide

Mole ratio Olefin/ Sulfide	Aziridines		Sulfurane (I)	Ratio
	Yields (%)	*trans* Isomer	Yield (%)	k_s/k_o
Olefin only	62.8	35.0	—	—
5	29.6	38.1	16.9	2.8
4	26.8	39.6	17.7	2.6
2	13.2	41.7	17.4	2.6
1	8.1	49.4	19.8	2.4
0.5	4.6	51.2	37.0	2.4
0.25	trace	*ca.* 70	44	—

Competitive reactions of dimethyl sulfide and *cis*-4-methyl-2-pentene towards the nitrene derived by the direct photolysis of methyl azidoformate were carried out. The results listed in Table 1 show the following tendencies in the relative rate between addition and iminosulfurane (I) formation, and in the stereochemistry of the addition to olefin. First, the relative rate constant of iminosulfurane (I) formation to addition k_s/k_o gradually decreased as the initial ratio of olefin and sulfide decreased. Secondly, although the yields of total aziridines decreased, the relative ratio of *trans* isomer increased as the initial concentration of sulfide increased. Even in the reaction with olefin alone, a considerable amount of *trans* aziridine was formed (*cis* : *trans*=2 : 1), that is to say, the addition is not strictly stereospecific. These tendencies can be best explained by assuming that the reaction of the singlet nitrene with solvent molecules competes with the intersystem crossing of the singlet to the triplet, and that the singlet adds to olefin stereospecifically and reacts with dimethyl sulfide giving iminosulfurane, while the triplet adds to olefin nonstereospecifically and reacts with the sulfide less easily without giving iminosulfurane. Increase in the initial concentration of sulfide will decrease the amount of aziridine derived from the singlet. This will diminish the probability of the intersystem crossing to give a less amount of the triplet nitrene and lower yields of the *trans* aziridine.

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