Tetrahedron Letters No. 19, pp 1921 - 1924, 1972. Pergamon Press. Printed in Great Britain.

PHOTOLYSIS AND PHOTOCHEMICAL PREPARATION OF IMINOSULFURANES: ON THE MULTIPLICITY OF NITRENES

Yoshiyuki Hayashi and Daniel Swern

Fels Research Institute and Department of Chemistry
Temple University, Philadelphia, Pennsylvania 19122

(Received in USA 14 March 1972; received in UK for publication 5 April 1972)

Recent papers on the photochemical preparation[1] of N-carbethoxyiminodialkylsulfuranes (1) and the photolysis[2] of N-benzoyliminodimethylsulfurane (2) in methanol prompt us to report our own findings on the photolysis and photochemical preparation of iminosulfuranes as well as additional information bearing on nitrene multiplicity.

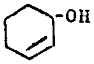
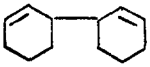
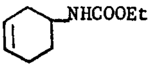
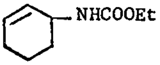
Photolysis of Iminosulfuranes. Carbethoxynitrene is probably the best known, most widely studied nitrene, conveniently generated by photolysis of ethylazidoformate (3).[3,4,5,6.] We have determined the yields, distribution and stereochemistry (where pertinent) of the reaction products obtained in the photolysis at 5-10° of N-carbethoxyiminodimethylsulfurane (1a), $(CH_3)_2S{=}NCOOEt$, in cyclohexene (Table I), cyclohexane (Table II) and cis- or trans-4-methyl-2-pentene (Table III), and have compared the results with those obtained on photolysis of 3 under the same conditions.

Photolysis of either 1a or 3 in cyclohexene gives similar ratios of 4:5:6:7 (Table I) but the yield of 7-carbethoxy-7-azabicyclo[4.1.0]heptane (4) is substantially lower (20%) from 1a than from 3 (49%). Carbethoxynitrene is presumably formed from both 1a and 3 on photolysis (no dark reaction occurs) but the basic question is the multiplicity of the nitrene from 1a. (Nitrene generated photochemically from 3 is estimated to consist of 2:1 singlet to triplet at 38° and 3:1 at 12°.[4])

The yields of 3,3'-biscyclohexenyl (8) and ethyl carbamate (9) are considerably higher from 1a than from 3 and suggest that 1a is producing a considerably higher proportion of triplet nitrene which is abstracting hydrogen atoms. This conclusion, based only on these limited results, must be regarded as tentative since the photosensitized decomposition of 3 gives even higher yields of 8 and 9 (63 and 74%, respectively) yet the formation of triplet nitrene in the photosensitized experiment seems to be excluded largely on the basis that triplet nitrene, if present, should have added to the double bond of cyclohexene, and essentially no double bond addition is observed.[4] (Bis(carbethoxyamino)methane (10) is usually formed in the thermal decomposition of 1a.[7])

1a was then photolyzed in cyclohexane and the results were compared with the photodecomposition of 3 in that solvent (Table II). Ethyl N-cyclohexylcarbamate (11), the C-H insertion product of singlet carbethoxynitrene, is obtained in only 21% yield from 1a whereas 9, the hydrogen abstraction product of triplet nitrene, is obtained in 57% yield. In contrast, 11 is obtained in 54% yield from 3 but 9 is obtained in only 4% yield. These results support our earlier tentative conclusion that the nitrene from 1a is largely triplet, and also confirm the

TABLE I--PHOTOLYSES IN CYCLOHEXENE[a]

Products	1a[b]	3[4]	
		Nonsensitized	Photosensitized
	Yield % (Product Ratio)	Yield % (Product Ratio)	Yield % (Product Ratio)
	small	-	-
 (8)	11	1-6	62.7
$H_2NCOOEt$ (9)	23	3	73.5
$CH_2(NHCOOEt)_2$ (10)	22	-	-
 (4)	20.4 (17)	49 (19)	1 (0.3)
 (5)	1.7 (1.4)	1 (0.4)	4 (1.1)
 (6)	1.2 (1.0)	2.6 (1.0)	3.5 (1.0)
 (7)	9.5 (7.9)	8.4 (3.2)	3 (0.9)

[a] The photolyses of Tables I, II and III were conducted under nitrogen using quartz reaction vessels and a Rayonet Photochemical Reactor (low pressure mercury lamps No. RPR-2537A) in a cold room at 0°. Structural assignments of all products are based on a comparison of their IR and NMR spectra and GLC retention times (if possible) with those of authentic compounds.

[b] Cyclohexene: Methylene chloride 5:1, 100 ml/2g of 1a. Reaction time 4 days (nitrogen atmosphere). A tarry precipitate formed on the walls during photolysis and only 70% of 1 was consumed.

literature suggestion that the nitrene from 3 is largely singlet.[3]

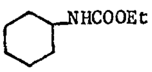
Another chemical criterion for assessing nitrene multiplicity is its stereoselectivity of addition to a *cis* or *trans* olefin, results of which are in Table III. As a control we repeated (and confirmed) the work of Lwowski and coworkers[4,5] who showed that singlet nitrene is the predominant species in the photolysis of 3 (and the exclusive product in its thermolysis[3,5]).

In contrast, photolysis of 1a to 10% decomposition in *cis*-4-methyl-2-pentene gave a 58:42 *cis/trans* ratio in only 14% yield (based on 1a consumed) and a 63% yield of 9. With the *trans* olefin, the *cis/trans* ratio of aziridines was 8:92 in 20% yield, accompanied by a 65% yield of 9. The conclusion is clear that the nitrene from 1a is largely triplet, clearly in excess of 50%.

Photochemical Preparation of Iminosulfuranes. When a solution of 3 (4g) is photolyzed at 5-10° in dimethyl sulfide (100 ml) under nitrogen for 24 hours, 40% of 3 decomposes (no dark reaction occurs). Vacuum evaporation of the excess sulfide at low temperature yields a residue of 1a and 3 whose NMR spectrum is virtually identical with that of pure 1a[7] dissolved in 3. Based on 3 consumed, the yield of 1a is 90-95%; short path distillation gives a 71% yield of pure 1a and recovery of the remaining 60% of 3. (Only singlet nitrene is reportedly trapped by sulfides.[1])

$$\underline{3} \quad + \quad x's\ Me_2S \quad \xrightarrow[5\text{-}10°;\ 24\ hrs.]{h\nu} \quad \underset{(40\%)}{1a} \quad + \quad \underset{(60\%)}{\underline{3}}$$

TABLE II--PHOTOLYSES IN CYCLOHEXANE

Products, Yield %		1a[a]	3[4]
	(11)	21	54
$H_2NCOOEt$	(9)	57	4
$CH_2(NHCOOEt)_2$	(10)	11	-

[a] Cyclohexene: Methylene chloride 2:1; 100 ml/2g of 1a. Reaction time 3 days (nitrogen atmosphere) and only 39% of 1a was consumed (tarry precipitate coated vessel wall).

TABLE III--PHOTOLYSES IN cis- OR trans-4-METHYL-2-PENTENE.[a]

Products	1a + cis-olefin	1a + trans-olefin	3 + cis olefin	3 + trans olefin
Aziridines, yield %	14	20	71	65
Aziridines, cis/trans ratio	58/42	8/92	70/30	6/94
$H_2NCOOEt$ (9), yield %	63	65	trace	2
$CH_2(NHCOOEt)_2$ (10), yield %	7	8	-	-

[a] 100 ml of hydrocarbon used per 2 g of 1a or 3. The former reaction system was heterogeneous throughout; reaction time was 1 day (nitrogen atmosphere) and only 10% of 1a was consumed (tarry precipitate coated vessel wall).

Yields of 1 reported by Ando and coworkers,[1] in contrast, were only 40-60% but since those were yields of isolated products, processing losses may explain the lower values. Another possibility is that higher reaction temperatures (unspecified by them) were used which would lower the singlet:triplet ratio. Alternatively, the formation of 1a may not require the intermediacy of a nitrene; dimethyl sulfide may be attacking excited 3 with elimination of nitrogen. This seems unlikely, however, in view of the facile decomposition of excited 3 to carbethoxynitrene and nitrogen.[3-6]

In contrast with 3, photolysis of benzoyl azide (60% decomposition) in dimethyl sulfide yields only 35% of 2.

$$\mathrm{PhCON_3} + \text{x's}\ \ \mathrm{Me_2S} \xrightarrow[5\text{-}10°,\ 48\ \text{hrs.}]{h\nu} \underset{(35\%)}{2} + \underset{(32\%)}{\mathrm{PhNCO}\ (12)} + \underset{(3\%)}{\mathrm{PhCONH_2}}$$

2 is photochemically unstable (compared to 1a) and undergoes concomitant decomposition to 12 and 13. The difference between the photodecomposition of 1a and 2 in methylene chloride is striking and clearly shows the influence of the PhCO moiety in 2.

$$1a \xrightarrow[5\text{-}10°,\ 72\ \text{hrs.}]{h\nu,\ \mathrm{CH_2Cl_2}} \underset{(6\%)}{\mathrm{CH_2(NHCOOEt)_2}} + \underset{(2\%)}{9} + \underset{(82\%)}{1a}$$

$$2 \xrightarrow[5\text{-}10°,\ 48\ \text{hrs.}]{h\nu,\ \mathrm{CH_2Cl_2}} \underset{(53\%)}{\overset{\mathrm{PhNCO}}{12}} + \underset{(9\%)}{\overset{\mathrm{PhCONHCONHPh}}{13}}$$

Transylidation. Photolysis of 1a (2g) in excess diethyl sulfide (50 ml) under nitrogen at 5-10° for 48 hours gives a mixture of 1a and N-carbethoxyiminodiethylsulfurane (1b) (no dark reaction occurs). In contrast, 2 under the same conditions undergoes considerably less transylidation and considerably more decomposition (see above also).

$$\underline{\text{1a}} \quad + \quad \text{x's} \quad Et_2S \quad \xrightarrow[\text{48 hours}]{h\nu,\ 5\text{-}10°} \quad \underset{(55\%)}{\underline{\text{1a}}} \quad + \quad \underset{(45\%)}{\underline{\text{1b}}}$$

$$\underline{2} \quad + \quad \text{x's} \quad Et_2S \quad \xrightarrow[\text{48 hours}]{h\nu,\ 5\text{-}10°} \quad \underset{(45\%)}{\underline{2}} \quad + \quad \underset{(15\%)}{PhCON{=}SEt_2} \quad + \quad \underset{(40\%)}{\text{other products}}$$

Since, as we have shown, the trapping of singlet nitrene by sulfides is a highly efficient process, it is quite possible that photolysis of 1a is yielding the singlet species initially but in relatively poor traps (cyclohexane, olefins) intersystem crossing prevails and we obtain considerable triplet reaction products in those cases, as we showed earlier (Tables I, II, III). The transylidation yield in the photodecomposition of 2 shows that at least one-fourth of the nitrene formed is singlet.

Acknowledgement: This paper, Iminosulfuranes IX, was supported in part by U.S. Public Health Service Grants CA-07803, 07174 and 08793 of the National Cancer Institute.

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