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THERMAL AND PHOTOCHEMICAL CURTIUS TYPE REARRANGEMENT OF N-ACYL-S,S-DIPHENYLSULFIMIDES

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Thermal decomposition of N-acyl-S,S-diphenylsulfimides(Ia-g) gave easily isocyanates(IIa-g) in high yields, together with diphenyl sulfide, while photolysis of Id afforded the insertion product(III), indicating the formation of singlet nitrene.

Recently, a number of workers reported preparative procedures and reactions of free sulfimides and their N-substituted derivatives.$^{1-9)}$ Meanwhile, N-benzoyl-S,S-diphenylsulfimide(Ie) is highly stable and does not decompose even on heating at 140°C for 24 h in such solvents as benzene, dioxane or toluene. However, when N-acyl-S,S-diphenylsulfimides(Ia-g) were heated in situ or in tetraline solution at about 200°C, they decomposed readily to afford the rearranged products, isocyanates and diphenyl sulfide, in high yields, unlike N-sulfonyl derivatives which are stable at 200°C for 24 h.

We wish to report the mode of the thermal decomposition of I under molten condition and the evidence that nitrene was not formed in the thermolysis of I, in comparison with the mode of the photolysis of Id.

When N-acyl-S,S-diphenylsulfimides(Ia-g)$^{10)}$ were heated under molten state in degassed sealed tubes at 200°C for 0.3-2 h, the corresponding isocyanates(IIa-g) were obtained in high yields, together with diphenyl sulfide. Furthermore, when the thermolysis of Ib and d was carried out in tetraline or benzene solution in a sealed tube, the products obtained were the corresponding isocyanate(IIb,d) and diphenyl sulfide and neither C-H insertion nor hydrogen abstraction product like as the corresponding acylamide could be obtained. The results are shown in Table 1. In order to examine if the nitrene is generated during the rearrangement, the thermolysis of Ib was carried out in the presence of excess diphenylacetylene under the same condition, since acylnitrenes have been proposed as intermediates in the Curtius rearrangement of carbonyl azides to isocyanates and some addition reactions of acylnitrenes to acetylenes, sulfoxides, and olefins have been reported.$^{11)}$ Furthermore, an intramolecular C-H insertion reaction or hydrogen abstraction of a certain nitrene has also been reported.$^{11)}$ However, the products obtained are the isocyanate(IIb) and diphenyl sulfide and neither addition products of phenylacetylnitrene nor hydrogen abstraction product could be detected. Meanwhile, acylnitrenes were reported as intermediates in the photolysis of acyl azides$^{11)}$ and acylsulfimides.$^{10,12)}$ In order to reconfirm the formation of a nitrene as an intermediate in the photolysis, Id was irradiated with 254 nm light in benzene or dichloromethane and the corresponding C-H insertion product(III) was obtained (36.8% in benzene, 25.4% in dichloromethane) together with IId(34.4% in benzene, 26.6% in dichloromethane). The yield of III decreased to ~0%, when Id was irradiated in the presence of benzophenone as the triplet sensitizer in dichloromethane solution, while IId was obtained in almost the same yield(25.6%) as in the absence of benzophenone. These results indicate that in the photolysis of Id the singlet nitrene is the actual intermediate for the formation of III.

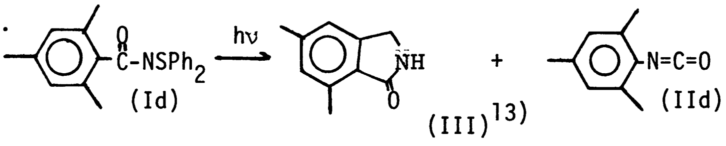
The facts that the addition product of Ib could not be obtained and neither the insertion nor hydrogen abstraction product with Id could be detected seem to rule out the possible formation of an acylnitrene as the intermediate in the thermal reaction of N-acyl-S,S-diphenylsulfimides. The pyrolysis of N-acyl-S,S-diphenylsulfimides provides a convenient route to prepare the corresponding isocyanates, since S,S-diphenylsulfimides can be readily prepared and are easily handled, unlike the azides.

Table 1. Yields of the Thermal Decomposition Products of Sulfimides(I)

$$\underset{(I)}{Ph_2SNCOR} \xrightarrow[\text{in molten state}]{200°C} \underset{(II)}{R\text{-}N{=}C{=}O} + \underset{(IV)}{Ph_2S}$$

R	Time (min)	Bp(°C) (Mp)	Yields(%) (II)	Yields(%) (IV)	IR(cm^{-1})	NMR($CDCl_3$)(δ)
Ia CH_3	60	37-38	67.5	91	2270	3.03(s,3H)
Ib $PhCH_2$	"	118/200mHg	90.4	96.8	2270	7.37(s,5H),4.50(s,2H)
Ib* "	"		92.6	94.7		
Ic $Ph(CH_2)_2$	"	104-106/15mmHg	86.6	94.4	2270	7.23(s,5H),3.57(t,2H) 2.90(t,2H)
Id Mesityl	20	(45-46)	95.5	95.6	2270	6.77(s,2H),2.23(s,9H)
Ie Ph	120	58.2-59.5/18mmHg	34.7**	85.7	2270	7.6-6.9(m,5H)
If EtCH(Ph)	60		98.8	98	2270	7.27(s,5H),4.50(t,1H) 2.07-1.50(m,2H),0.97(t,3H)
Ig Adamantyl	"	135-136	97.6	98	2270	2.30-1.50(m,15H)

* In the presence of excess diphenyl acetylene. ** Dimerized product of phenyl isocyanate was obtained.



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13) III, Mp 165-167°C. IR(KBr),3180,3060,1690. NMR(δ $CDCl_3$),6.97(s,2H),4.30(s,2H),2.64(s,3H), 2.36(s,3H). Correct elemental analyses were obtained.

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