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SULFOXIMIDOYL RADICAL. HOMOLYTIC ADDITION OF N-HALOSULFOXIMIDES TO OLEFINS

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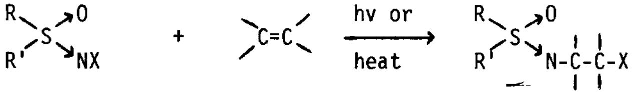
Homolytic addition reaction of N-halosulfoximides, i.e., diphenyl-N-chloro sulfoximide(1), diphenyl-N-bromosulfoximide(2), and methylphenyl-N-chloro-sulfoximide(3), to such olefins as tert-butylethylene and cyclohexene was found to afford the corresponding N-alkylated sulfoximides, which are presumed to be formed via the initial addition of the sulfoximidoyl radical.

Aminyl radicals or acylaminyl radicals generated from the corresponding N-haloamines or N-haloamides, e.g., succinimidoyl radical, are known to react with olefins to afford either the 1,2-addition products or allylic halogenated products.[1)] Since N-chlorosulfoximide is an effective chlorinating agent,[2)] similar to N-chlorosuccinimide, it is expected to react with olefins. Thus, we have carried out both thermal and photochemical decompositions of N-halosulfoximides[3)] in the presence of olefins, and found that treatment of N-halosulfoximides with olefins under both ultraviolet irradiation and thermolysis in the presence of radical initiator afforded the corresponding 1,2-addition products in moderate yields (Scheme 1). We now wish to communicate the first example of the facile radical-chain addition of N-halosulfoximides to olefins.

Scheme 1.



(R,R'=Ph,Ph or Me,Ph, X=Cl or Br)

The addition reaction was carried out using a 10 : 1 molar ratio of olefin/N-chloro-sulfoximide(1) in methylene chloride as solvent (0.2 M in N-chlorosulfoximide) in a degassed sealed tube. The reaction was initiated either photochemically through Pyrex using a high pressure mercury arc lamp as a light source or thermally in the presence of α,α'-azobisisobutyronitrile (AIBN) at 80°C; both methods were effective and the yield of the adduct was ca.50%. In the absence of the initiator no reaction occured. Products were separated by column chromatography packed with silica gel using chloroform as an eluent or by preparative thin layer chromatography coated with silica gel using ether as an eluent while their structures were determined by spectroscopic and elemental analyses. The results obtained are summarized in Table 1.

Table 1. Reaction of 1 with tert-Butylethylene

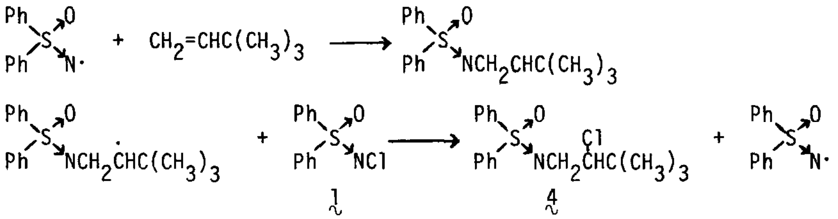
Run	Heat or hv	Temp(°C)	Time(h)	Added Materials	Products and Yields(%)a)(GLC analysis) Adduct(4)	 N-unsubstituted Sulfoximide
1	hv	0	3	-	50.9	44.2
2	hv	0	3	p-quinone 10%	8.6	trace
3	dark	r.t.	24	-	0	0
4	heat	80	5	-	2.3	trace
5	heat	80	5	AIBN 5%	49.2(44.7)b)	42.8(42.0)b)
6	heat	80	5	AIBN 5% p-quinone 10%	1.5	trace
7	hv	-15	3	-	51.3	41.7
8	hv	20	3	-	56.1	39.9

a) The yields are based on 1. b) Isolated yields are shown in parentheses.

The adduct (diphenyl-N-(β-chloro-γ,γ-dimethyl)butylsulfoximide(4)) has three coupling constants in nmr (J=3.0, 9.5, 13.1Hz) centered at δ=4.0, 3.60, 3.08ppm, indicating that this addition reaction proceeded via trans-addition of N-chlorosulfoximide(1) to tert-butylethylene. When the adduct(4) was reduced with tri-n-butyltin hydride in the presence of AIBN, diphenyl-N-(γ,γ-dimethyl)butylsulfoximide was obtained, indicating that the sulfoximide group is combined to the terminal carbon atom of tert-butylethylene.

As shown in Table 1, the yield of the adduct(4) was negligible without irradiation or radical initiator but increased remarkably by ultraviolet irradiation or in the presence of a radical initiator (AIBN), and dropped down to negligible again in the presence of a radical scavenger (p-quinone). The addition reaction did not proceed at all in the dark, while no rearranged products was observed in the reaction of tert-butylethylene, seemingly ruling out any ionic reaction mechanism. These observations clearly indicate that the addition product is formed by a chain sequence involving the sulfoximidoyl radical as shown in Scheme 2.

Scheme 2.



The yield of 4 was not influenced by the change of the reaction temperature between -15 to 20°C, though it was reported that in the reaction of N-bromoacetamide with cyclohexene the yiel of the adduct increased when the reaction temperature was lowered.[4)]

Meanwhile, 1 was found to be reduced readily with tri-n-butyltin hydride to the corresponding N-unsubstituted sulfoximide and tin chloride, as in the homolytic reduction of diphenyl N-chloroketimine with tri-n-butyltin hydride involving the ketimino radical as the chain carrier. This observation also seems to suggest the facile formation of the sulfoximidoyl radical as the intervening intermediate in the reduction of 1.

Similar additions of N-halosulfoximides to other olefins were carried out. The results obtained are given in Table 2.

Table 2. Reaction of N-Halosulfoximides with Olefins

N-Halo-sulfoximide	Olefin	Reaction Conditions Solvent,Heat or hv,Temp,Time	Products and Yields(%)*) Adduct	N-unsubstituted Sulfoximide
$Ph_2S(O)NCl$ (1)	$CH_2=CHC(CH_3)_3$	CH_2Cl_2, 80°C, 5h, AIBN 5%	44.7	42.0
		CH_2Cl_2, hv, 0°C, 3h	53.7	46.3
$Ph_2S(O)NBr$ (2)	$CH_2=CHC(CH_3)_3$	benzene, hv, 0°C, 4h	21.9	54.9
$Ph(Me)S(O)NCl$ (3)	$CH_2=CHC(CH_3)_3$	CH_2Cl_2, hv, 0°C, 3h	58.5	38.7
$Ph_2S(O)NCl$	cyclohexene	CH_2Cl_2, hv, 0°C, 3h	28.5	60.8
$Ph_2S(O)NBr$	cyclohexene	CH_2Cl_2, hv, 0°C, 4h	22.5	59.9
$Ph_2S(O)NCl$	$CH_3CH=C(CH_3)_2$	CH_2Cl_2, hv, 0°C, 3h	26.5	36.9
$Ph_2S(O)NCl$	1-octene	CH_2Cl_2, hv, 0°C, 5h	22.0	46.1
$Ph_2S(O)NCl$	benzene	benzene, hv, 0°C, 3h	0	-
$Ph_2S(O)NBr$	benzene	CH_2Cl_2, hv, 0°C, 4h	0	-
	benzene	CH_2Cl_2, 80°C, 5h, AIBN 5%	0	quant.
$Ph_2S(O)NCl$	trans-PhCH=CHPh	CH_2Cl_2, 80°C, 5h, AIBN 5%	0	64.5

*) Isolated yields.

Other N-halosulfoximides, **2** and **3**, also add to tert-butylethylene affording the corresponding 1 : 1 adducts. The reactions of **1** with other olefins such as 2-methyl-2-butene or cyclohexene afforded the similar corresponding products, while with trans-stilbene no adduct was obtained. Under the similar reaction conditions benzene and other aromatic hydrocarbons are quite inert. In the reaction of **2** with cyclohexene, however, 3-bromocyclohexene was obtained in 50.6% yield together with the adduct(22.5%), although no allylic halogenation product was obtained in the reaction of **1** with cyclohexene. Therefore, the allylic bromination of cyclohexene is considered to proceed via a chain process involving bromine molecule like the "Goldfinger mechanism"6), but not via that involving the sulfoximidoyl radical.7) These results reveal clearly that the sulfoximidoyl radical can act as an electrophilic radical to afford 1 : 1 adduct to nucleophilic olefin such as tert-butylethylene.

References and Footnotes

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3) N-Halosulfoximides, **1**, **2**, and **3** were prepared from the halogenation of the corresponding N-unsubstituted sulfoximides with aqueous sodium hypochlorite or aqueous sodium hydroxide-bromine solution.

4) D. Touchard and J. Lessard, Tetrahedron Lett., 4425 (1971); D. Touchard and J. Lessard, ibid., 3827 (1973).

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7) The sulfoximidoyl radical seems to have less ability of hydrogen abstraction from allylic compound, i.e., cyclohexene.

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