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HOMOLYTIC HALOGENATION OF TOLUENE WITH N-HALOSULFOXIMIDES

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Homolytic bromination of toluene with diphenyl N-bromosulfoximide (**1**) proceeded readily by ultraviolet irradiation or by thermal reaction in the presence of a radical initiator to afford benzyl bromide. However, chlorination of toluene was sluggish with diphenyl N-chlorosulfoximide (**2**) and methyl phenyl N-chlorosulfoximide (**3**). α-Bromination was interpreted in terms of a chain process involving bromine molecule like the "Goldfinger mechanism", but not via that involving the sulfoximidoyl radical.

N-Halosulfoximides prepared by halogenation of the corresponding N-unsubstituted sulfoximides readily react with sulfides or phosphines affording either the corresponding sulfonium or phosphonium derivatives.1) Earlier, the N-chlorosulfoximide (**3**) was shown to be an effective chlorinating agent2) similar to N-chlorosuccinimide. Meanwhile, homolytic halogenation with N-haloamines or N-haloamides is known to afford either the 1,2-addition products or allylic hydrogen abstraction products.3) Recently, we found that N-halosulfoximides react with olefins to afford the corresponding 1 : 1 addition products via a chain process involving the sulfoximidoyl radical.4) In order to extend the scope of halogenation with N-halosulfoximides, we have carried out thermal and photochemical halogenations of toluene with N-halosulfoximides, and found that when toluene was treated with N-bromosulfoximide (**1**) under ultraviolet irradiation or thermolysis in the presence of a radical initiator, benzyl bromide was obtained in high yields, but in the reaction of N-chlorosulfoximides (**2** and **3**), benzyl chloride was obtained in low yields.

Generally the reaction was carried out with the N-halosulfoximide (0.1 mmol) and toluene (0.5 mmol) dissolved in 1 ml of methylene chloride in a degassed sealed tube. The reaction was initiated with either photochemically through Pyrex using a high pressure mercury arc lamp as a light source at 0°C or thermally in the presence of α,α'-azobisisobutyronitrile (AIBN) at 80°C. In the absence of the initiator no thermal reaction occured. Products were separated through chromatography column packed with silica gel using chloroform as an eluent and identified by means of spectroscopic and gas-chromatographic analyses. The results obtained are summarized in Table.

Inspection of the Table reveals an interesting feature of halogenation of toluene with N-halosulfoximides (**1**, **2** and **3**). At room temperature the reaction did not proceed at all without ultraviolet irradiation and the N-halosulfoximides were recovered quantitatively, however upon ultraviolet irradiation of the methylene chloride solution of toluene and N-bromosulfoximide (**1**), bromination proceeded nicely to afford benzyl bromide in a substantial yield. The yield of benzyl bromide decreased slightly in the presence of a radical scavenger (p-quinone). When the reaction mixture was heated at 80°C, bromination proceeded substantially even without the radical initiator, while the effect of the radical scavenger was very small. Meanwhile chlorination with 2 or 3 either

Table. Reaction of N-Halosulfoximides with Toluene

N-Halo-sulfoximide	Reaction Conditions$^{1)}$					Products and Yields(%)$^{2)}$		
	heat or hv,	temp, (°C)	time, (h)	Added Material		$PhCH_2X$	N-unsubstituted sulfoximide	recovered N-halo-sulfoximide
$Ph_2S(O)NBr$ (1)	-	20	24	-	X:Br	0	0	100$^{3)}$
	hv	0	5	-		75.4	87.6	0
	hv	0	5	p-quinone 10%		59.6	88.5	0
	heat	80	5	-		74.9	85.0	0
	heat	80	5	AIBN 5%		84.8	93.0	0
	heat	80	5	BPO 5%		79.5	89.0	0
	heat	80	5	p-quinone 10%		75.4	83.5	0
	heat	80	5	AIBN 5% p-quinone 10%		82.5	92.3	0
	heat	80	5	BPO 50%		86.0	95.0	0
$Ph_2S(O)NCl$ (2)	-	20	24	-	X:Cl	0	0	100$^{3)}$
	hv	0	5	-		2.8	13.0	-
	heat	80	3	AIBN 5%		5.0	7.2	82.0
	heat	80	5	BPO 50%		62.5	69.1$^{3)}$	20.0$^{3)}$
Ph(Me)S(O)NCl (3)	-	20	24	-	X:Cl	0	0	100$^{3)}$
	hv	0	3	-		7.5	21.8$^{3)}$	67.7$^{3)}$
	heat	80	5	-		5.1	6.5	80.7
	heat	80	5	AIBN 5%		4.3	7.1	81.7
	heat	80	5	AIBN 5% p-quinone 10%		0	3.8	90.0

1) N-Halosulfoximide:toluene=1:5. 2) The yields are based on N-halosulfoximide and determined by GLC. 3) Isolated yields.

by photolysis or by thermal initiation in the presence of the radical initiator was sluggish and the yield of benzyl chloride was only few per cent, while no aromatic substitution took place. When an equimolar amount of the radical initiator (BPO 50%) was used, the yield of benzyl chloride was moderately increased.

These observations resemble nicely that in the reaction of 1 with cyclohexene, 3-bromocyclohexene was obtained in 50.6% yield together with the 1,2-addition product (diphenyl N-2-bromocyclohexylsulfoximide, 22.5%), however, no allylic halogenation product was obtained in the reaction of 2 with cyclohexene.$^{4)}$ Thus N-bromosulfoximide (1) is considered to generate bromine molecule upon contacting with hydrogen bromide formed during the reaction and bromine molecule is considered to be the active brominating reagent in this bromination. Indeed, in the reaction of 1 with cyclohexene, 1,2-dibromocyclohexane was found to be obtained in 8.1% yield upon careful product analysis.$^{4)}$ Apparently the sulfoximidoyl radical has no ability of hydrogen abstraction and hence cannot act as a chain carrier in halogenation of toluene with N-halosulfoximides. α-Bromination of toluene with 1 is considered to proceed via a chain process involving bromine molecule like the "Goldfinger mechanism"$^{5)}$ as in bromination of allylic compounds with N-bromosuccinimide,$^{3b)}$ but not via that involving the sulfoximidoyl radical.

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