Homolytic Reaction of *N*-Halogenosulphoximides with Olefins and Toluene

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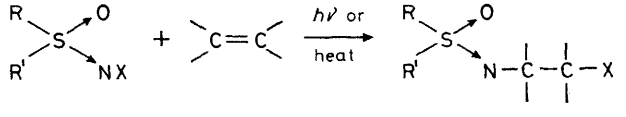
Homolytic addition reaction of *N*-halogenosulphoximides, *i.e.* diphenyl-*N*-chlorosulphoximide (1), diphenyl-*N*-bromosulphoximide (2), and methylphenyl-*N*-chlorosulphoximide (3), to olefins such as t-butylethylene and cyclohexene under both u.v. irradiation and thermolysis in the presence of a radical initiator was found to afford the corresponding *N*-alkylated sulphoximides, which are presumed to be formed *via* the initial addition of the sulphoximidoyl radical. Meanwhile, homolytic bromination of toluene with *N*-bromosulphoximide (2) proceeded readily by u.v. irradiation, or by thermal reaction in the presence of a radical initiator, to afford benzyl bromide. However, chlorination of toluene was sluggish with *N*-chlorosulphoximides (1) and (3). α-Bromination was interpreted in terms of a chain process involving bromine molecules like the ' Goldfinger mechanism,' but not *via* that involving the sulphoximidoyl radical.

N-HALOGENOSULPHOXIMIDES [1,2] prepared by halogenation of the corresponding *N*-unsubstituted sulphoximides readily react with such nucleophiles as sulphides or phosphines affording the corresponding sulphonium or phosphonium derivatives. Earlier, the *N*-chlorosulphoximide (3) was shown to be an effective chlorinating agent [3] toward aziridines and sulphoxides similar to *N*-chlorosuccinimide. Meanwhile, homolytic halogenation with *N*-halogenoamines or *N*-halogenoamides is known to afford either the 1,2-addition product, *e.g.* β-halogenoamine derivatives, or 3-halogeno-olefins which are formed upon allylic hydrogen abstraction.[4] Thus, we carried out both thermal and photochemical decompositions of *N*-halogenosulphoximides in the presence of olefins, and found that treatment of *N*-halogenosulphoximides with olefins under both u.v. irradiation, and thermolysis, in the presence of a radical initiator, afforded the corresponding 1,2-addition products *via* a chain process involving the sulphoximidoyl radical.[5]



(1); R = R' = Ph, X = Cl

(2); R = R' = Ph, X = Br

(3); R = Ph, R' = Me, X = Cl

SCHEME 1

Moreover, in order to extend the scope of halogenation with *N*-halogenosulphoximides, we carried out thermal and photochemical halogenations of toluene with *N*-halogenosulphoximides, and found that upon u.v. irradiation or thermolysis of toluene, with *N*-bromosulphoximide (2) in the presence of a radical initiator, benzyl bromide was obtained in high yields, but in the reaction of *N*-chlorosulphoximides (1) and (3), benzyl chloride was obtained in low yields.[6]

This paper describes these homolytic reactions of *N*-halogenosulphoximides with olefins and toluene, and discusses the nature of the sulphoximidoyl radical.

RESULTS AND DISCUSSION

Homolytic Addition of N-*Halogenosulphoximides to Olefins.*—*N*-Halogenosulphoximides (1), (2), and (3) were prepared by halogenation of the corresponding *N*-unsubstituted sulphoximides with aqueous sodium hypochlorite or aqueous sodium hydroxide–bromine solution according to the procedure reported earlier.[2] The addition reaction was carried out using a 10 : 1 molar ratio of olefin : *N*-chlorosulphoximide (1) in methylene chloride as solvent (0.2M in *N*-chlorosulphoximide) in a degassed sealed tube. The reaction was initiated either photochemically through Pyrex glass using a high-pressure mercury-arc lamp as a light source or thermally in the presence of αα'-azobisisobutyronitrile (AIBN) at 80 °C; both methods were effective and the yield of the adduct was *ca.* 50%. In the absence of the initiator the thermal reaction did not proceed at all. Products were separated by column chromatography packed with silica gel using chloroform for elution or by preparative t.l.c. coated with silica gel using ether for elution, while their structures were determined by spectroscopic and elemental analyses. The results obtained are summarized in Table 1.

When the adduct, diphenyl-*N*-[(2-chloro-3,3-dimethyl)butyl]sulphoximide (4), was reduced with tri-n-butyltin hydride in the presence of AIBN, diphenyl-*N*-[(3,3-dimethyl)butyl]sulphoximide (5) was obtained, indicating that the sulphoximide-group is combined to the terminal carbon atom of t-butylethylene in an anti-Markovnikov orientation.

As shown in Table 1, the yield of the adduct (4) was negligible without irradiation or in the presence of a radical initiator but increased remarkably upon u.v. irradiation or thermolysis in the presence of a radical initiator. Furthermore, upon u.v. irradiation or thermolysis in the presence of a radical scavenger, *i.e.* *p*-quinone, the yield of the adduct (4) dropped down to 8.6 and 1.5% from 50.9 and 49.2%, respectively. These results, namely the non-occurrence of addition reaction in the dark and the lack of any rearranged product in the reaction of t-butylethylene, seem to rule out any ionic

TABLE 1

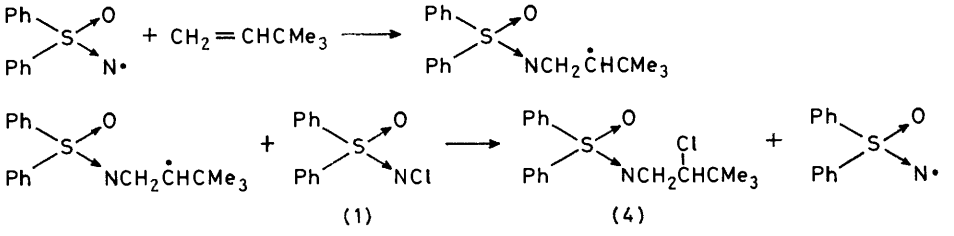
Reaction of (1) with t-butylethylene

Run	Heat or *hν*	Temp. (°C)	Time (h)	Added materials	Products and yields (%) [a] Adduct (4)	*N*-unsubstituted-sulphoximide
1	*hν*	0	3		50.9	44.2
2	*hν*	0	3	*p*-quinone (10%)	8.6	Trace
3	dark	Ambient	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	*hν*	−15	3		51.3	41.7
8	*hν*	20	3		56.1	39.9

[a] The yields are based on (1) by g.l.c. analysis. [b] Isolated yields are shown in parentheses.

reaction pathway; however, they indicate clearly that the addition product is formed *via* a chain sequence involving the sulphoximidoyl radical as shown in Scheme 2.

The yield of the adduct (4) seemed to depend on the concentration of *N*-chlorosulphoximide (1) [in 0.5M and 0.2M concentration, (4) was obtained in 56.0 and 30.0% isolated yields, respectively] and this trend in the formation of the adduct resembles the addition reaction of *N*-halogenosuccinimides to olefins.[4c,f] The yield of (4) was also not influenced by the change of the reaction temperature in the range between −15 to 20 °C, though in the reaction of *N*-bromoacetamide with cyclohexene the yield of the adduct was reported to increase when the reaction temperature was lowered.[7]



SCHEME 2

Meanwhile, (1) was found to be reduced readily with tri-n-butyltin hydride to the corresponding *N*-unsubstituted sulphoximide 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.[8] This observation also seems to suggest the facile formation of the sulphoximidoyl radical as the intervening intermediate in the reaction of (1).

Similar additions of *N*-halogenosulphoximides to other olefins were also carried out. The results obtained are listed in Table 2.

Other *N*-halogenosulphoximides, (2) and (3), were also found to add to t-butylethylene affording the corresponding 1 : 1 adducts. The reactions of (1) with other olefins such as 2-methylbut-2-ene or cyclohexene afforded the corresponding addition products, while with *trans*-stilbene no adduct was obtained. The adduct, diphenyl-*N*-(2-chlorocyclohexyl)sulphoximide (9), has two coupling constants in the n.m.r. spectrum (J 4.4 and 9.0 Hz) centred at δ 4.02 and 3.08, indicating that this addition reaction proceeded *via trans*-addition of *N*-

TABLE 2

Reaction of *N*-halogenosulphoximides with olefins

N-Halogenosulphoximide	Olefin	Reaction conditions: Solvent, heat or *hν*, temperature, time	Products and yields (%) * adduct	*N*-Unsubstituted-sulphoximide
$Ph_2S(O)NCl$ (1)	CH_2=$CHCMe_3$	CH_2Cl_2, 80 °C, 5 h, AIBN (5%)	44.7 (4)	42.0
		CH_2Cl_2, *hν*, 0 °C, 3 h	53.7 (4)	46.3
$Ph_2S(O)NBr$ (2)	CH_2=$CHCMe_3$	benzene, *hν*, 0 °C, 4 h	21.9 (6)	54.9
$Ph_2S(O)NBr$	CH_2=$CHCMe_3$	CH_2Cl_2, *hν*, 0 °C, 4 h	36.8 (6)	41.5
$Ph(Me)S(O)NCl$ (3)	CH_2=$CHCMe_3$	CH_2Cl_2, *hν*, 0 °C, 3 h	58.5 (7)	38.7
$Ph_2S(O)NCl$	cyclohexene	CH_2Cl_2, *hν*, 0 °C, 3 h	28.5 (8)	60.8
$Ph_2S(O)NBr$	cyclohexene	CH_2Cl_2, *hν*, 0 °C, 4 h	22.5 (9)	59.9
$Ph_2S(O)NCl$	CH_3CH=CMe_2	CH_2Cl_2, *hν*, 0 °C, 3 h	26.5 (10)	36.9
$Ph_2S(O)NCl$	oct-1-ene	CH_2Cl_2, *hν*, 0 °C, 5 h	22.0 (11)	46.1
$Ph_2S(O)NCl$	benzene	benzene, *hν*, 0 °C, 3 h	0	
$Ph_2S(O)NBr$	benzene	CH_2Cl_2, *hν*, 0 °C, 4 h	0	
	benzene	CH_2Cl_2, 80 °C, 5 h, AIBN (5%)	0	Quantitative
$Ph_2S(O)NCl$	*trans*-PhCH=CHPh	CH_2Cl_2, 80 °C, 5 h, AIBN (5%)	0	64.5

* Isolated yields.

chlorosulphoximide (1) to cyclohexene. Under similar reaction conditions benzene and other aromatic hydrocarbons are quite inert. In the reaction of (2) with cyclohexene, however, 3-bromocyclohexene and 1,2-dibromocyclohexene were obtained in 50.6 and 8.1% yields, respectively, together with the adduct (9) in 22.5% yield, although no allylic halogenation product was obtained in the reaction of (1) with cyclohexene. The allylic bromination of cyclohexene is considered to proceed *via* a chain process involving bromine molecules according to the ' Goldfinger mechanism ',[9] but not *via* that involving the sulphoximidoyl radical. The sulphoximidoyl radical does not seem to abstract allylic hydrogen of olefins, *e.g.* cyclohexene, but can act as an electrophilic radical to add to such a nucleophilic olefin as t-butylethylene to afford the 1 : 1 adduct.

TABLE 3

Reaction of *N*-halogenosulphoximides with toluene

N-Halogenosulphoximide [a]	Solvent	Heat or *hν*	Temp. (°C)	Time/h	Added materials		Products and yields (%) [b] PhCH$_2$X	*N*-Unsubstituted-sulphoximide	Recovered *N*-halogenosulphoximde
Ph$_2$S(O)NBr (2)	CH_2Cl_2		20	24		X : Br	0	0	100 [c]
	CH_2Cl_2	*hν*	0	5			75.4	87.6	0
	CH_2Cl_2	*hν*	0	5	*p*-quinone (10%)		59.6	88.5	0
	Benzene	heat	80	5			74.9	85.0	0
	Benzene	heat	80	5	AIBN (5%)		84.8	93.0	0
	Benzene	heat	80	5	BPO (5%)		79.5	89.0	0
	Benzene	heat	80	5	*p*-quinone (10%)		75.4	83.5	0
	Benzene	heat	80	5	AIBN (5%) *p*-quinone (10%)		82.5	92.3	0
	Benzene	heat	80	5	BPO (50%)		86.0	95.0	0
Ph$_2$S(O)NCl (1)	CH_2Cl_2		20	24		X : Cl	0	0	100 [c]
	CH_2Cl_2	*hν*	0	5			2.8	13.0	
	CH_2Cl_2	heat	80	3	AIBN (5%)		5.0	7.2	82.0
	CH_2Cl_2	heat	80	5	BPO (50%)		62.5	69.1 [c]	20.0 [c]
Ph(Me)S(O)NCl (3)	CH_2Cl_2		20	24		X : Cl	0	0	100 [c]
	CH_2Cl_2	*hν*	0	3			7.5	21.8 [c]	67.7 [c]
	CH_2Cl_2	heat	80	5			5.1	6.5	80.7
	CH_2Cl_2	heat	80	5	AIBN (5%)		4.3	7.1	81.7
	CH_2Cl_2	heat	80	5	AIBN (5%) + *p*-quinone (10%)		0	3.8	90.0

[a] *N*-Halogenosulphoximide : toluene = 1 : 5. [b] The yields are based on *N*-halogenosulphoximide and determined by g.l.c. [c] Isolated yields.

Homolytic Halogenation of Toluene with N-*Halogenosulphoximides*.—The halogenation of toluene (0.5 mmol) was carried out with the *N*-halogenosulphoximide (0.1 mmol) in methylene chloride (1 ml) in a degassed sealed tube. The reaction was initiated either photochemically through Pyrex glass using a high-pressure mercury-arc lamp as a light source at 0 °C, or thermally in the presence of AIBN at 80 °C. In the absence of the initiator no thermal reaction occurred. Products were separated on a chromatography column packed with silica gel using chloroform for elution, and identified by means of spectroscopic and gas-chromatographic analyses. The results obtained are summarized in Table 3.

Inspection of Table 3 reveals an interesting feature of halogenation of toluene with the *N*-halogenosulphoximides (1), (2), and (3). At room temperature the reaction did not proceed at all without u.v. irradiation and the *N*-halogenosulphoximides were recovered quantitatively; however, upon u.v. irradiation of a methylene chloride solution of toluene and *N*-bromosulphoximide (2), bromination proceeded smoothly to afford benzyl bromide in 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 (1) or (3), either by photolysis or by thermal initiation in the presence of the radical initiator, was sluggish and the yield of benzyl chloride was only a few percent, while no aromatic substitution took place. When an equimolar amount of the radical initiator benzoyl peroxide (BPO) (50%) was used, the yield of benzyl chloride increased moderately.

These observations appear to be similar to those observed in the reaction of (2) with cyclohexene, where though 3-bromocyclohexene was obtained in 50.6% yield together with the 1,2-addition product [(9), 22.5%], no allylic halogenation product was obtained in the reaction of (1) with cyclohexene. Thus *N*-bromosulphoximide (2) is considered to generate, by reaction with hydrogen bromide formed during the reaction, bromine molecules, which are the active brominating reagent in this bromination. Indeed, in the reaction of (2) with cyclohexene, 1,2-dibromocyclohexene was found to be obtained in 8.1% yield upon careful product analysis, indicating clearly that bromine molecules are generated during the reaction. Here again the sulphoximidoyl radical was found to be incapable of hydrogen abstraction from toluene, and hence unable to be a chain carrier in halogenation of toluene with *N*-halogenosulphoximides. α-Bromination of toluene with (2) is considered to proceed *via* a chain process involving bromine molecules according to the ' Goldfinger mech-

anism '[9] as in the bromination of allylic compounds with *N*-bromosuccinimide,[4e,f] but not *via* that involving the sulphoximidoyl radical.

EXPERIMENTAL

The i.r. spectra were recorded on a Hitachi 215 spectrometer, while the n.m.r. spectra of the compounds in deuteriated chloroform were recorded on a Hitachi–Perkin-Elmer R-20 high-resolution or a Bruker FXD 4-100 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained on a Hitachi RMU-6MG mass spectrometer (20 eV). G.c.–mass spectra were taken on the same spectrometer equipped with a 2-m × 4-mm internal diameter glass column packed with Silicon OV-1 on 60—80 mesh Chromosorb W (AW). Preparative column chromatography was performed with silica gel (Wakogel C-300) using chloroform as eluant. Preparative thin layer chromatography was performed on Merck PF_{254} silica gel plates 2 mm thick using ether for elution. G.l.p.c. analysis was performed with a Hitachi 163 gas chromatograph with a flame ionization detector, equipped with a 1-m × 4-mm internal diameter stainless steel column packed with Silicon GE SE-30 on 60—80 mesh Chromosorb W (AW). U.v. irradiation was carried out in a degassed sealed tube through Pyrex glass using a Riko-sha HL-400J high-pressure mercury-arc lamp as a light source. Spectroscopic data for compounds (4)—(12) are deposited as SUP 22731 (3 pp.).* Analytical data for compounds (4)—(12) are in Table 4.

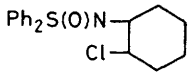
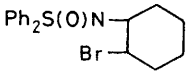
Diphenyl-*N*-chlorosulphoximide (1) and methylphenyl-*N*-chlorosulphoximide (3) were prepared according to the procedure reported earlier, starting from the corresponding *N*-substituted sulphoximide with aqueous sodium hypochlorite;[2] (1), m.p. 149—150 °C (lit.,[2b] 149.5—150.0 °C), $\nu_{max.}$ (KBr) 1 235, 1 090, and 965 cm^{-1}: (3), m.p. 88—89 °C, $\nu_{max.}$ (KBr) 1 225, 1 090, 990, and 935 cm^{-1}. Diphenyl-*N*-bromosulphoximide (2) was prepared as follows: diphenyl-*N*-unsubstituted-sulphoximide (1 g, 4.6 mmol) and sodium hydroxide (0.22 g, 5.5 mmol) were dissolved in methanol (10 ml). To this solution was added a methanolic solution of bromine (0.88 g, 5.5 mmol) at 0 °C. The solution was stirred at 0 °C for 10 min, then poured into ice–water. The pale yellow precipitate was collected, washed with water, and dried, yield 95%, m.p. 158—159 °C; $\nu_{max.}$ (KBr) 1 230, 1 085, and 970 cm^{-1}.

The commercially available olefins were used without purification. All solvents used were purified before use.

*Reaction of Diphenyl-*N*-chlorosulphoximide* (1) *with t-Butylethylene.*—Compound (1) (252 mg, 1 mmol) and t-butylethylene (840 mg, 10 mmol) were dissolved in methylene chloride (5 ml). The mixture was placed in a degassed sealed tube, which was irradiated through Pyrex glass using a high-pressure mercury-arc lamp at 0 °C for 3 h; the sealed tube was then broken, and the solvent and olefin were removed *in vacuo*. The residue was separated by preparative t.l.c. Diphenyl-*N*-[(2-chloro-3,3-dimethyl)-butyl]sulphoximide (4) was obtained in 30% yield, together with diphenyl-*N*-unsubstituted-sulphoximide (56.0%). Compound (4) was identified by i.r., n.m.r., and mass spectra and elemental analyses; m.p. 121—122 °C (from hexane). When 2 ml of methylene chloride was used as solvent, (4) and diphenyl-*N*-unsubstituted-sulphoximide were obtained in 53.7 and 46.3% yields, respectively. The results obtained are shown in Table 4.

TABLE 4

Elemental analyses of the adduct

Adduct		M.p. (°C)	Formula	Analytical data (Calc.) Found
$Ph_2S(O)NCH_2CH(Cl)CMe_3$ (4)		121—122	$C_{18}H_{22}NClOS$	(C, 64.4, H, 6.6, N, 4.2) C, 64 2, H, 6.6, N, 4.2
$Ph_2S(O)NCH_2CH_2CMe_3$ (5)		50—51	$C_{18}H_{23}NOS$	(C, 71.7, H, 7.7, N, 4.6) C, 71.5, H, 7.5, N, 4.5
$Ph_2S(O)NCH_2CH(Br)CMe_3$ (6)		125—126	$C_{18}H_{22}NBrOS$	(C, 56.8, H, 5.8, N, 3.7) C, 57.1, H, 5.8, N, 3.6
$Ph(Me)S(O)NCH_2CH(Cl)CMe_3$ (7)		Oil	$C_{13}H_{20}NClOS$	(C, 57.0, H, 7.4, N, 5.1) C, 56.8, H, 7.2, N, 5.3
	(8)	139—140	$C_{18}H_{20}ClOS$	(C, 64.8, H, 6.0, N, 4.2) C, 64.9, H, 6.0, N, 4.2
	(9)	112—113		
PhS(O)NCH(Me)–$CClMe_2$ (10)		81—82	$C_{17}H_{20}NClOS$	(C, 63.4, H, 6.3, N, 4.4) C, 64.0, H, 6.2, N, 4.4
$Ph_2S(O)NCH_2$–CH(Cl)$[CH_2]_5Me$ (11)		Oil		

*Reaction of Diphenyl-*N*-chlorosulphoximide* (1) *with t-Butylethylene under Varying Conditions.*—Compound (1) (1.01 g, 4 mmol) and t-butylethylene (3.36 g, 40 mmol) were dissolved in methylene chloride (20 ml). 2-ml Portions of this solution was placed in sealed Pyrex glass tubes after degassing. In some tubes, a third component (5% AIBN or/and 10% *p*-quinone) was added. Each tube was allowed to stand at 80 °C for 5 h or irradiated through Pyrex glass using a high-pressure mercury-arc lamp at several temperatures for 3 h. Then the sealed tube was broken and 1 μl of the reaction mixture was directly injected into a g.l.c. column to determine the amounts of (4) and diphenyl-*N*-unsubstituted-sulphoximide. The yields obtained are shown in Table 1.

*Reduction of Diphenyl-*N*-[(2-chloro-3,3-dimethyl)butyl]-sulphoximide* (4) *with Tri-n-butyltin Hydride.*—Compound (4) (190 mg, 0.57 mmol), tri-n-butyltin hydride (198 mg,

* For details see Notice to Authors No. 7, *J.C.S. Perkin I*, 1979, Index issue.

0.68 mmol), and AIBN (8 mg, 0.057 mmol) were dissolved in benzene (5 ml). The mixture was allowed to stand in an atmosphere of argon at 80 °C for 5 h. The solvent was then removed *in vacuo* and the products were chromatographed through a column packed with silica gel using chloroform for elution. Diphenyl-*N*-[(3,3-dimethyl)butyl]sulphoximide (5) was obtained in 80.0% yield together with diphenyl-*N*-unsubstituted-sulphoximide (5.0%) and the starting compound (4) (10.0%), m.p. 50—51 °C.

*Reduction of Diphenyl-*N*-chlorosulphoximide* (1) *with Tri-n-butyltin Hydride.*—Compound (1) (126 mg, 0.5 mmol), tri-n-butyltin hydride (146 mg, 0.5 mmol), and AIBN (4 mg, 0.025 mmol) were dissolved in benzene (5 ml). The mixture was allowed to stand in an atmosphere of argon at 80 °C for 3 h. The solvent was then removed *in vacuo* and the residue was chromatographed through a column packed with silica gel using chloroform for elution. Diphenyl-*N*-unsubstituted-sulphoximide and tri-n-butyltin chloride were obtained in 99.5 and 81.1% yields, respectively. The products were identified by comparison of their i.r. and n.m.r. spectra with those of the authentic samples.

Reaction of N*-Halogenosulphoximides* (1), (2), *and* (3) *with Several Olefins.*—A typical run was as follows. Compound (2) (296 mg, 1 mmol) and t-butylethylene (840 mg, 10 mmol) were dissolved in methylene chloride (3 ml). The mixture was placed in a degassed sealed tube, which was irradiated through Pyrex glass using a high-pressure mercury-arc lamp at 0 °C for 4 h. Then the sealed tube was broken, and the solvent and olefin were removed *in vacuo*. The products obtained were separated by preparative t.l.c. Diphenyl-*N*-[(2-bromo-3,3-dimethyl)butyl]sulphoximide (6) was obtained in 36.8% yield together with diphenyl-*N*-unsubstituted-sulphoximide (41.5%), m.p. 125—126 °C (from hexane). Thermal reaction was carried out by heating at 80 °C for 5 h in the presence of 5% AIBN.

All the other reactions were carried out as described above. The spectral data and elemental analyses are summarized in Tables 2 and 4, and in SUP 22731.

*Reaction of Diphenyl-*N*-bromosulphoximide* (2) *with Cyclohexene.*—Compound (2) (296 mg, 1 mmol) and cyclohexene (820 mg, 10 mmol) were dissolved in methylene chloride (3 ml). The mixture was placed in a degassed sealed tube, which was irradiated through Pyrex glass using a high-pressure mercury-arc lamp at 0 °C for 4 h. The sealed tube was then broken and 1 μl of the reaction mixture was directly injected into a g.l.c. column to determine the amounts of low-boiling-point products. 3-Bromocyclohexene and 1,2-dibromocyclohexane were obtained in 50.6 and 8.1% yields, respectively. These structures were determined by gas-chromatographic and spectroscopic analyses. The rest of the reaction mixture was evaporated *in vacuo* and the residue was separated by preparative t.l.c. Diphenyl-*N*-(2-bromocyclohexyl)sulphoximide (9) and diphenyl-*N*-unsubstituted-sulphoximide were obtained in 22.5 and 59.9% yields, respectively. The results obtained are shown in Table 4. In the reaction of (1) with cyclohexene, 3-chlorocyclohexene was not detected by g.l.c. analysis.

Reactions of N*-Halogenosulphoximides* (1), (2), *and* (3) *with Toluene.*—A typical run was as follows. Compound (1) (141 mg, 0.74 mmol) and toluene (340 mg, 3.7 mmol) were dissolved in methylene chloride (2 ml). The mixture was placed in a degassed sealed tube, which was irradiated through Pyrex glass using a high-pressure mercury-arc lamp at 0 °C for 3 h. Then the sealed tube was broken and 1 μl of the reaction mixture was directly injected into a g.l.c. column to determine the amount of benzyl chloride (7.5% yield). The solvent and toluene of the rest of the reaction mixture were removed *in vacuo*. The residue was chromatographed through a column packed with silica gel using chloroform for elution. Compound (1) was recovered in 67.7% yield, together with benzyl chloride and diphenyl-*N*-unsubstituted-sulphoximide (21.8%).

Compound (2) (207 mg, 0.7 mmol) and toluene (322 mg, 3.5 mmol) were dissolved in benzene (7 ml). 1-ml Portions of the benzene solution were placed in a degassed sealed tube. In some tubes, a third component (5% AIBN or/and 10% *p*-quinone) was added. The thermal reaction was carried out by heating at 80 °C for 5 h. The reaction mixture was then worked up as in the photolysis.

All the other reactions were also carried out similarly and the results obtained are summarized in Table 3.

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