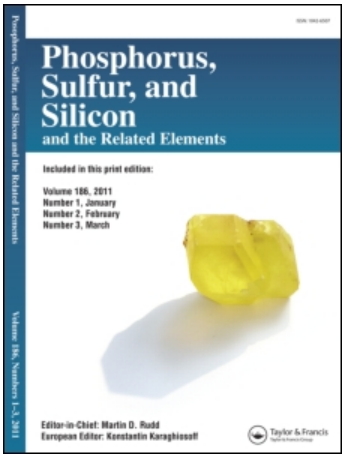

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REACTION OF *N*-HALOSULFOXIMINES WITH DISULFIDES

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The reaction of *S,S*-diphenyl-*N*-chloro-(**1**), *S,S*-diphenyl-*N*-bromo-(**2**), and *S*-methyl-*S*-phenyl-*N*-chlorosulfoximine (**5**) with disulfides in refluxing carbon tetrachloride was found to afford the corresponding sulfoxides. In the presence of pyridine, **1** and **2** reacted with disulfides at room temperature to give the corresponding bis-diphenylsulfoximinyl alkyl or aryl sulfonium halides arising from the reaction of the intermediary *N*-sulfenylated sulfoximine and the starting *N*-halosulfoximine.

INTRODUCTION

The chemistry of sulfoximines has been explored largely with *N*-unsubstituted sulfoximines and their *N*-alkylated or *N*-acylated derivatives.[1] Only a few examples of *N*-heteroatom-substituted sulfoximines are known. Rees and his co-workers have prepared a series of *N*-aminosulfoximines from the corresponding *N*-aminolactams by oxidation with lead tetraacetate in the presence of sulfoxides.[2] The reaction has been used to synthesize optically active *N*-phthaliminosulfoximines in high yields from optically active sulfoxides.[3] It has been reported that *N*-chloro-[4] and *N*-bromosulfoximines[5] were prepared by chlorination and bromination of the corresponding *N*-unsubstituted sulfoximines with various halogenating agents. These *N*-halosulfoximines are very reactive and, upon treatment with sulfides or phosphines, afforded either the corresponding *N*-sulfonio- or *N*-phosphoniosulfoximines,[6] or upon treatment with sodium *p*-toluenethiolate in the presence of a crown ether, afforded the corresponding *N*-(α-toluenesulfenyl)sulfoximine.[7]

It is also known that the reactions of *N*-bromoimides, e.g., *N*-bromosuccinimide, with disulfides in the presence of such catalysts as pyridine or benzoyl peroxide (BPO) give the corresponding *N*-sulfenylated imides (sulfenimides) in high yields.[8] Also, *S*-methyl-*S*-phenyl-*N*-chlorosulfoximine was shown to be an effective chlorinating agent toward aziridines[9] and sulfoxides[10] in a manner similar to *N*-chlorosuccinimide. Furthermore, homolytic reactions of *N*-halosulfoximines with olefins initiated by ultraviolet irradiation and thermolysis in the presence of a radical initiator afforded the corresponding 1 : 1 adducts, e.g., *S,S*-diphenyl-*N*-(2-chloro-3,3-dimethyl)butylsulfoximine, via a facile radical-chain reaction involving the sulfoximinyl radical.[5b] As an extension of these works, the reaction of *N*-halosul-

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foximines with disulfides was carried out with an aim to obtain the corresponding *N*-sulfenylated sulfoximines.

This paper describes the results obtained from the reaction of *N*-halosulfoximines with disulfides under several conditions.

RESULTS AND DISCUSSION

N-Halosulfoximine, i.e., *S,S*-diphenyl-*N*-chloro-(**1**) or *S,S*-diphenyl-*N*-bromosulfoximine (**2**), was treated with dibenzyl disulfide in refluxing carbon tetrachloride for 30 min. The corresponding *N*-(α-toluenesulfenyl)sulfoximine was not obtained at all, but the reduced product, i.e., diphenyl sulfoxide, was obtained in moderate yield [(**1**); 55.3%, (**2**); 80.4%] together with *S,S*-diphenylsulfoximine.[11] The results obtained from the reaction of *S,S*-diphenyl-*N*-halosulfoximines with disulfides under several conditions are summarized in Table I.

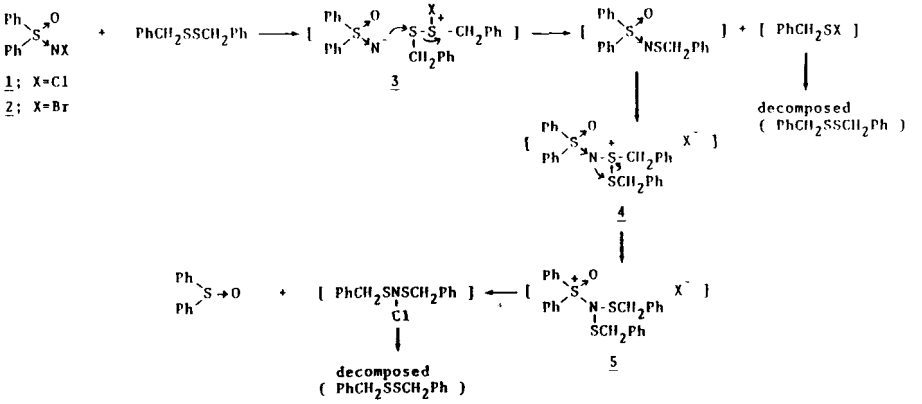
As shown in Table I, the reduction was not influenced by either the presence or absence of a radical initiator (5% BPO) or a radical scavenger (10% p-quinone). The reduction of *N*-halosulfoximines did not proceed at all in the absence of disulfides, even in the presence of 5% BPO.[5b] The yield of the sulfoxides seems to be independent of the concentration of dibenzyl disulfide and this evidence suggests that disulfide is regenerated and serves as a catalyst.[12] The sulfoximinyl radical intermediate[5b] does not decompose to afford the sulfoxide under the present conditions. *S,S*-Diphenylsulfoximine was not reduced at all. These observations suggest that the reaction may proceed via the ionic process as shown in Scheme 1.

Since it has been demonstrated that *N*-halosulfoximines generate a reactive halogen atom,[5a,9,10] the reaction may initially proceed via a nucleophilic attack by

TABLE I

Reaction of *S,S*-diphenyl-*N*-halosulfoximines with disulfides under several conditions

N-Halosulfoximine	Disulfide	Additives	Products and Yields (%) Ph_2SO	$Ph_2S(O)NH$	recovered disulfide	recovered-(**1**)
$Ph_2S(O)NCl$ (**1**)	$(PhCH_2S)_2$	—	55.3	22.9	78.5	10.0
$Ph_2S(O)NBr$ (**2**)	$(PhCH_2S)_2$	—	80.4	—	64.3	—
1	$(PhCH_2S)_2$	5% benzoyl peroxide	50.7	8.1	64.3	11.0
1	$(PhCH_2S)_2$	10% p-quinone	52.2	10.5	72.7	9.0
1	$(PhCH_2S)_2$ 0.5eq	—	59.5	15.0	68.3	—
1	$(phCH_2S)_2$ 0.2eq	—	47.9	24.0	—	—
1	$(PhS)_2$	—	23.5	28.2	73.0	29.3
1	$(CH_3S)_2$	—	42.3	30.4	—	18.5
1	—	—	0	—	—	93.0
1	—	5% BPO	0	—	—	91.0
$Ph_2S(O)NH$	$(PhCH_2S)_2$	—	0	quant.	—	—
$Ph_2S(O)NH$	—	5% BPO	0	quant.	—	—

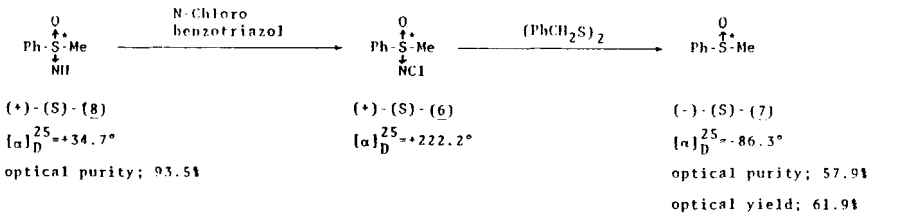


SCHEME 1

the sulfur atom of the disulfide on the halogen atom of the *N*-halosulfoximine forming an intermediate (**3**) followed by substitution on the sulfenyl sulfur atom of the intermediate (**3**) by the imino-nitrogen atom of the sulfoximine affording the *N*-sulfenylated sulfoximine and sulfenyl halide. In the subsequent step in which **4** might be formed and rearrange, the intermediate (**5**) would be obtained but decompose through the attack of halide anion on the nitrogen atom, eventually giving rise to the sulfoxide analogous to the reaction of *N*-unsubstituted sulfoximine with elemental sulfur and disulfides.[11c] This reaction mechanism seems to be supported by the earlier observations that the reaction of *N*-halosulfilimines with sulfides afforded the corresponding sulfiliminosulfonium salts ($Ph_2S{=}N{-}\overset{+}{S}R_2X^-$) via an initial attack of sulfide on the halogen atom of the *N*-halosulfilimine forming the halosulfonium salt ($Ph_2S{=}N^-X{-}\overset{+}{S}R_2$), followed by substitution on the sulfur atom of the sulfonium salt by the sulfilimino anion.[13]

Moreover, in order to shed light on this mechanism, the reaction of optically active *S*-methyl-*S*-phenyl-*N*-chlorosulfoximine (**6**) with dibenzyl disulfide was carried out and the results obtained are shown in Scheme 2.

Inspection of the data summarized in Scheme 2 reveals that the reaction proceeded with net retention around the sulfur atom with partial racemization. *S*-Methyl-*S*-phenylsulfoximine hydrochloride ($Ph(Me)S(O)\overset{+}{N}H_2Cl^-$) was obtained in 5.2% yield together with methyl phenyl sulfoxide ((**7**), 17.9% yield), suggesting that



SCHEME 2

TABLE II

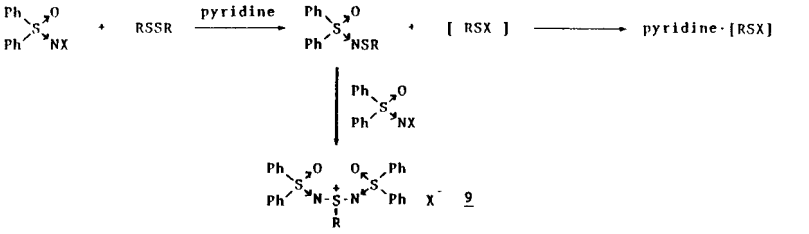
Reaction of *S,S*-diphenyl-*N*-halosulfoximines wih disulfides in the presence of pyridine

N-Halosulfoximine	Disulfide	*N*-Halosulfoximine:[a] Disulfide: Pyridine	Products and Yields (%)	
			$(Ph_2S(O)N)_2\overset{+}{S}RX^-$ **9**	$Ph_2S(O)NSR$ **10**
$Ph_2S(O)NCl$ (**1**)	$(PhCH_2S)_2$	1 : 3 : 3	44.0(Cl^-)	11.9
1	$(CH_3S)_2$	1 : 3 : 3	55.3(ClO_4^-)	—[b]
1	$(p\text{-TolS})_2$	1 : 2 : 3	67.7(ClO_4^-)	6.0
$Ph_2S(O)NBr$ (**2**)	$(PhCH_2S)_2$	1 : 2 : 2	51.2(Br^-)	—[b]

[a] Molar ratio.
[b] Not isolated.

hydrogen chloride is generated during the reaction and catalyzes the partial racemization of the sulfoxide (**7**).[14] Recently, reductive deimination of optically active *S*-methyl-*S*-phenylsulfoximine (**8**) with *tert*-butylthionitrite also resulted in the partial racemization of the corresponding sulfoxide indicating that acidic NO or NO_2 catalyzed the partial racemization of the sulfoxide.[15] Thus, all these results seem to support the mechanistic pathway shown in Scheme 1 and the configuration around the sulfur atom of sulfoxide formed should be the same as that of the sulfoximine. Furthermore, if the sulfenyl chloride generated during the reaction could be removed from the reaction mixture, the *N*-sulfenylated sulfoximine must be obtained as an intermediate which may also indicate the proposed mechanism as shown in Scheme 1. Therefore, *N*-halosulfoximines were treated with disulfides in the presence of pyridine.[8a] In the reaction with dibenzyl disulfide, bis-diphenylsulfoximinylbenzylsulfonium chloride (**9**; R = $PhCH_2$) was obtained in 44% yield, and was identified by means of spectroscopic and elemental analyses as the perchlorate prepared by treatment with sodium perchlorate. *S,S*-Diphenyl-*N*-(α-toluenesulfenyl)sulfoximine (**10**; R = $PhCH_2$) was also obtained in 11.9% yield together with *S,S*-diphenylsulfoximine (39.2%). The results are summarized in Table II.

The results seem to suggest that initial sulfenylation of *N*-halosulfoximines takes place since *N*-sulfenylsulfoximine was obtained, albeit in low yield. The main products are bis-diphenylsulfoximinyl alkyl or aryl sulfonium salts (**9**) which are new diazasulfonium salts. It may be considered that these salts come from the reaction of *N*-sulfenylsulfoximines with the starting *N*-halosulfoximines (Scheme 3). The nitrogen atom of the *N*-sulfenylated sulfoximine serves as the nucleophilic center[16] which attacks the halogen atom of *N*-halosulfoximine to form the intermediate ($Ph_2S(O)N-\overset{+}{S}(Cl)R\overset{-}{N}S(O)Ph_2$) followed by substitution on the sulfur atom by $Ph_2S(O)N$ to afford the final product. In order to confirm these processes, *S,S*-diphenyl-*N*-(α-toluenesulfenyl)sulfoximine (**10**) was treated with *N*-chlorosulfoximine (**1**). Bis-diphenylsulfoximinylbenzylsulfonium chloride (**9**) was actually obtained in 52.7% yield. These results indicate clearly that the formation of bis-diphenylsulfoximinyl alkyl or aryl sulfonium salts proceeds via the *N*-sulfenylated sulfoximine.



SCHEME 3

EXPERIMENTAL

All the melting points are uncorrected. The ir spectra were recorded on a Hitachi 215 Spectrometer; the ^{1}H-NMR spectra of the compounds in deuterated chloroform were recorded with a Hitachi Perkin-Elmer R-20 High Resolution NMR spectrometer using tetramethylsilane as an internal standard.

S,S-Diphenyl-*N*-chloro-(**1**) and *S,S*-diphenyl-*N*-bromosulfoximine (**2**) were prepared according to the procedure reported earlier.[4b,5b] Optically active *S*-methyl-*S*-phenyl-*N*-chlorosulfoximine [(+)-(S)-(**6**), $[\alpha]_D^{25} = +222.2°$ (c, 0.90, acetone)] was prepared starting from the corresponding *N*-unsubstituted sulfoximine[11c,17] [(+)-(S)-(**8**), $[\alpha]_D^{25} = -34.7°$ (c, 1.50, acetone), optical purity; 93.5%] with *N*-chlorobenzotriazole according to the method used by Montanari.[9] The commercially available disulfides were purified by recrystallization or distillation before use.

Reaction of N-Halosulfoximines with Disulfides. *S,S*-Diphenyl-*N*-chlorosulfoximine (**1**) 100 mg (0.4 mmol) and dibenzyl disulfide 98 mg (0.4 mmol) were dissolved in 4 ml of carbon tetrachloride and the mixture was refluxed for 30 min. The solvent was removed *in vacuo* and the residue was separated by preparative thin layer chromatography (Merck PF_{254} silica gel plates 2 mm thick) coated with silica gel using ether for elution. Diphenyl sulfoxide and *S-S*-diphenylsulfoximine were obtained in 55.3 and 22.9% yields, respectively, together with recovered (**1**) (10%) and dibenzyl disulfide (78.5%). The structures of the products were determined by comparison of their ir and ^{1}H-NMR spectra and melting points with those of the authentic samples. In the reaction of *N*-bromosulfoximine (**2**) with dibenzyl disulfide under the same condition, diphenyl sulfoxide was obtained in 80.4% yield together with dibenzyl disulfide (64.3%).

The reaction of **1** with dibenzyl disulfide in the presence of 5% benzoyl peroxide afforded the following products; products and yields (%), diphenyl sulfoxide (50.7), *S,S*-diphenylsulfoximine (8.1), recovered (**1**) (11.0), and dibenzyl disulfide (64.3), in the presence of 10% p-quinone; diphenyl sulfoxide (52.2), *S,S*-diphenylsulfoximine (10.5), recovered (**1**) (9.0), and dibenzyl disulfide (72.7). When **1** was heated in refluxing carbon tetrachloride for 30 min in the absence or presence of 5% benzoyl peroxide, the starting material was recovered in more than 90% yield. *S,S*-Diphenylsulfoximine was not reduced at all upon heating in the presence of dibenzyl disulfide or 5% benzoyl peroxide.

All other reactions were carried out in the same manner as mentioned above and the results obtained are shown in Table I.

Reaction of (+)-(S)-S-Methyl-S-phenyl-N-chlorosulfoximine (**6**) *with Dibenzyl Disulfide.* **6** $[[\alpha]_D^{25} = +222.2°$ (c, 0.90, acetone)] 190 mg (1 mmol) and dibenzyl disulfide 246 mg (1 mmol) were dissolved in carbon tetrachloride (12.5 ml) and the mixture was refluxed for 30 min. Chloroform (10 ml) was added to the reaction mixture and the insoluble precipitates were collected. *S*-Methyl-*S*-phenylsulfoximine hydrochloride was obtained in 5.2% yield. The solvent was removed *in vacuo* and the residue was separated by preparative thin layer chromatography using ether for elution. (−)-(S)-Methyl phenyl sulfoxide (**7**) was obtained in 17.9% yield $[[\alpha]_D^{25} = -86.3°$ (c, 0.25, acetone), optical purity; 57.9%, optical yield; 61.9%] together with *S*-methyl-*S*-phenylsulfoximine ((**8**), 16.1%).

Reaction of N-Halosulfoximines with Disulfides in the Presence of Pyridine. A typical run was as follows: Dibenzyl disulfide 738 mg (3 mmol) and pyridine 237 mg (3 mmol) were dissolved in 5 ml of benzene. To this solution was added 10 ml of benzene solution of **1** 252 mg (1 mmol) at room temperature. The solution was stirred at room temperature for 14 hours, then white precipitates deposited were collected, washed with water, and dried. These precipitates were identified as bis-diphenylsulfoximinyl benzyl sulfonium chloride ((**9**; R = $PhCH_2$, 44.0% yield) by means of spectroscopic analyses, mp 148.0–149.0°C (dec), recrystallized from ethanol-hexane. IR(KBr) ν 1225, 1095, and 975 cm^{-1} (O=S=N); NMR δ 7.95–8.20 (m, 4 H, o-PhH), 7.40–7.85 (m, 21 H, aromatic-H), and 5.62 (s, 2 H, $C\underline{H}_2Ph$) ppm. This

compound was dissolved into aqueous methanol solution and an excess of sodium perchlorate was added. A white precipitate was collected and dried. Bis-diphenylsulfoximinyl benzyl sulfonium perchlorate was obtained, mp 213.0–214.0°C (dec), recrystallized from methanol. IR(KBr) ν 1260, 1100, and 980 cm^{-1} (O=S=N); NMR (DMSO-d_6) δ 7.50–8.10 (m, 25 H, aromatic-H), 5.28 (s, 2 H, C$\underline{H}_2$Ph) ppm, Found: C, 56.68; H, 4.10; N, 4.41%. Calcd for $C_{31}H_{27}N_2ClO_6S_3$: C, 56.82; H, 4.15; N, 4.27%. The solvent and pyridine of the solution were removed *in vacuo*. The products obtained were separated by preparative thin layer chromatography using ether for elution. *S,S*-Diphenyl-*N*-(α-toluenesulfenyl)sulfoximine (**10**; R = $PhCH_2$) was obtained in 11.9% yield together with *S,S*-diphenylsulfoximine (39.2%), mp 134.0–135.0°C, recrystallized from benzene–hexane. IR(KBr) ν 1225, 1080, 1060, 1000, and 960 cm^{-1} (O=S=N); NMR δ 7.70–8.10 (m, 4 H, o-PhH), 7.35–7.70 (m, 10 H, aromatic-H), and 4.20 (s, 2 H, C$\underline{H}_2$Ph) ppm.

Reaction of **1** *with Dimethyl Disulfide.* Bis-diphenylsulfoximinyl methyl sulfonium perchlorate (**9**; R = Me), 55.3% yield, mp 209.0–210.0°C, recrystallized from chloroform–ether. IR(KBr) ν 1240, 1220, 1090, and 950 cm^{-1} (O=S=N); NMR(DMSO-d_6) δ 7.60–8.20 (m, 20 H, aromatic-H) and 3.58 (s, 3 H, CH_3) ppm. Found: C, 51.72; H, 3.84; N, 4.77%. Calcd for $C_{25}H_{23}N_2ClO_6S_3$: C, 51.85; H, 4.00; N, 4.83%.

Reaction of **1** *with Di-p-tolyl Disulfide.* Di-p-tolyl disulfide 492 mg (2 mmol) and pyridine 237 mg (3 mmol) were dissolved in 10 ml of benzene. To this solution was added 5 ml of benzene solution of **1** 252 mg (1 mmol) with stirring at room temperature. After 1 day, the solvent was removed by decantation and the residual oily precipitates were dissolved into aqueous hydrochloric acid solution and extracted with chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo*. Bis-diphenylsulfoximinyl p-tolyl sulfonium perchlorate (**9**; R = $PhCH_2$) (after exchanging counter anion with sodium perchlorate) was obtained in 67.7% yield (viscous oil). IR(neat) ν 1240, 1091, and 960 cm^{-1} (O=S=N); NMR δ 7.50–8.30 (m, 24 H, aromatic-H) and 2.50 (s, 3 H, p-CH_3) ppm. The benzene solution was washed with aqueous hydrochloric acid solution and dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, the residue was separated by preparative thin layer chromatography using ether for elution. *S,S*-Diphenyl-*N*-(α-toluenesulfenyl)sulfoximine was obtained in 6.0% yield together with recovered **1** (20.6%), mp 105.0–106.0°C, recrystallized from benzene–hexane. IR(KBr) ν 1230, 1095, 1010, and 950 cm^{-1} (O=S=N); NMR δ 7.85–8.25 (m, 4 H, aromatic-H), 7.15–7.85 (m, 10 H, aromatic-H), and 2.40 (s, 3 H, p-CH_3) ppm. Found: C, 66.99; H, 5.04; N, 3.96%. Calcd for $C_{19}H_{17}NOS_2$: C, 67.22; H, 5.04; N, 4.12%.

Reaction of **2** *with Dibenzyl Disulfide.* Dibenzyl disulfide 197 mg (0.8 mmol) and pyridine 63 mg (0.8 mmol) were dissolved in 3 ml of benzene. To this solution was added 2 ml of a benzene solution of **2** 118 mg (0.4 mmol) at room temperature. After 1 hr, the solvent was removed by decantation and yellow precipitates were collected, washed with water, and dried. Bis-diphenylsulfoximinyl benzyl sulfonium bromide was obtained in 51.2% yield, mp 137.0–138.0°C (dec), recrystallized from ethanol. IR(KBr) ν 1250, 1090, and 970 cm^{-1} (O=S=N); NMR δ 7.90–8.20 (m, 4 H, aromatic-H), 7.30–7.90 (m, 21 H, aromatic-H), and 5.58 (s, 2 H, CH_2Ph) ppm. Found: C, 58.68; H, 4.36; N, 4.55%. Calcd for $C_{31}H_{27}N_2BrO_2S_3$; C, 58.58; H, 4.28; N, 4.41%. The yields of diphenyl sulfoxide (1.6%), recovered **2** (6.3%), and *S,S*-diphenylsulfoximine (5.0%) obtained from the benzene solution were determined by means of high pressure liquid chromatography (Yanako L-1030 column, 0.2 × 50 cm; Gel-5510; carried, methanol).

Reaction of **10** (*R = CH_2Ph*) *with* **1**. **10** (R = CH_2Ph) 15 mg (0.045 mmol) and **1** 11 mg (0.045 mmol) were dissolved in 0.5 ml of benzene. This solution was kept to stand at room temperature for 1 day. Bis-diphenylsulfoximinyl benzyl sulfonium chloride **9** (R = CH_2Ph) was obtained in 52.7% yield. The structure of this compound was determined by comparison of its mp, ir and ^{1}H-NMR spectra with those of authentic sample.

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