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CHLORINATION OF PHENYLTHIOCYCLOPROPANES AND PHENYLSULFINYLCYCLOPROPANES WITH CHLORINATING AGENTS: PREPARATION OF 1-CHLORO-1-(PHENYLTHIO)CYCLOPROPANES AND 1-CHLORO-1-(PHENYLSULFINYL)CYCLOPROPANES$^{1)}$

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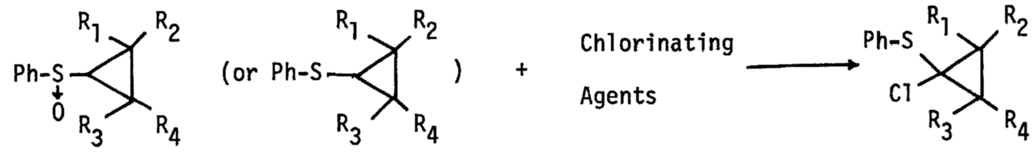
1-Chloro-1-(phenylthio)cyclopropanes and 1-chloro-1-(phenylsulfinyl)cyclopropanes are readily prepared by the direct chlorination of phenylthiocyclopropanes or phenylsulfinylcyclopropanes with various chlorinating agents.

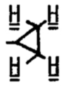
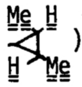
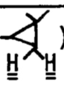
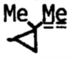
Various alkylthio- or arylthiocyclopropanes,$^{2)}$ arylsulfinylcyclopropanes,$^{3)}$ and related cyclopropyl compounds$^{4)}$ have recently been prepared. These compounds were employed either for new organic syntheses or for investigations on the characteristic features of cyclopropyl ring.$^{3,4,5)}$ Recently we found that the Pummerer reaction of phenylsulfinylcyclopropanes with acetic anhydride afforded the corresponding 1-acetoxy-1-(phenylthio)cyclopropanes in high yields without ring opening.$^{6)}$ Meanwhile, the solvolysis of 1-chloro-1-(phenylthio)cyclopropanes gave a concomitant mixture of both the unrearranged solvolysis products and the ring opening allylic products.$^{5,6)}$ These two experiments prompted us to investigate further the chemical behavior of the cyclopropyl ring attached to thio or sulfinyl groups. Thus, we have carried the Pummerer type chlorinations of phenylsulfinylcyclopropanes with thionyl chloride and propionyl chloride and phenylthiocyclopropanes with N-chlorosuccinimide(NCS),$^{7)}$ expecting to obtain some ring opening products due to the facile formation of chlorosulfonium complex. However, these chlorinations afforded the corresponding 1-chloro-1-(phenylthio)cyclopropanes in good yields. We wish to describe the results and their implication on understanding of the mechanisms of the reactions together with a few additional chlorinations of phenylsulfinylcyclopropanes with other chlolinating agents.

Preparation of 1-Chloro-1-(phenylthio)cyclopropanes(**2a**-c).$^{8)}$ Generally, secondary α-chlorosulfides cannot be readily prepared by the Pummerer type reaction of the corresponding sulfoxides either with thionyl chloride or acyl chloride, since α-chlorosulfides decompose readily to give various

Table I. Preparation of 1-Chloro-1-(phenylthio)cyclopropanes(2a-c)



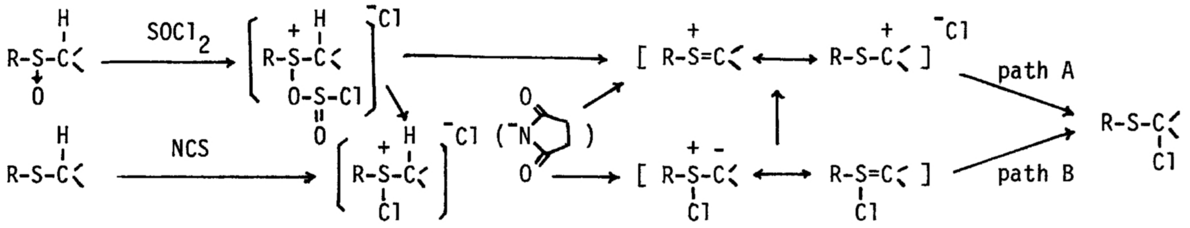
(1a-c) (3a-c) (2a-c)

Starting Materials (1a-c) or (3a-c)	R_1	R_2	R_3	R_4	Chlorinating Agents	Reaction Conditions	Products(2a-c)			
								Yields (%)	Bp(bath temp.) ($^{\circ}C/_{mmHg}$)(Lit.)	NMR Spectra (δ) ($CDCl_3$)
1a	H	H	H	H	$SOCl_2$	in CH_2Cl_2 at reflux for 1 h	2a	Quant.	$^{84}/_{3}$	1.3-1.6(m,4H, ), 7.0-7.6 (m,5H,Ph-S-)
1a	H	H	H	H	EtCOCl		2a	Quant.		
1b	Me	H	H	Me	$SOCl_2$		2b	85	$^{115}/_{1}$	1.0-1.5(m,8H, ),7.0-7.6 (m,5H,Ph-S-)
1c	Me	Me	H	H	$SOCl_2$		2c	71*	$^{115}/_{1}$($^{85-87}/_{0.2}$)2b)	1.2(q,2H, ), 1.33 and 1.44(s,3H and s,3H,  and ), 7.0-7.5(m,5H,Ph-S-)
3a	H	H	H	H	NCS	in benzene at room temperature for overnight	2a	90		
3b	Me	H	H	Me	NCS		2b	81		
3c	Me	Me	H	H	NCS		2c	82		

* 2,2-Dimethyl-1-(phenylthio)cyclopropane(3c) was obtained in 14% yield.

compounds. However unexpectedly, 1-chloro-1-(phenylthio)cyclopropanes(2), which we obtained by the present experiments, are quite stable under the reaction conditions (see Table I). The reaction was carried out as follows. To a solution of 3 mmol of phenylsulfinylcyclopropane(1) in 10 ml of dichloromethane was added a 1.2 mol excess of thionyl chloride (or propionyl chloride) in 10 ml of dichloromethane. After refluxing the mixture at room temperature for 2 h, it was poured into 50 ml of 5% aqueous sodium carbonate. The product(2) was purified further by distillation *in vacuo* (by bulb to bulb distillation).

The Pummerer type reaction has generally been considered to proceed via the formation of a carbonium ion intermediate which is stabilized by the sulfur atom8) (see path A). However, the lack of any ring opening product suggests that the reactions do not proceed via the mechanistic route which involves the carbonium ion intermediate, since the methanolysis5) or acetolysis6) of the 1-chloro-1-(phenylthio)cyclopropane gave the ring opening product which arises from the cyclopropyl carbonium cation as the intermediate. Therefore, these reactions are considered to proceed via a similar pathway as that of the phenylsulfinylcyclopropane with acetic anhydride,$^{6)}$ namely via the formation of the ylide - ylene intermediate (see path B).

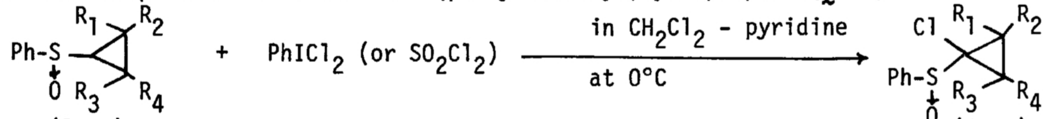


Meanwhile, in the reaction of phenylthiocyclopropanes(3) with NCS in benzene, 1-chloro-1-(phenylthio)cyclopropanes(2) were also obtained in good yields (see Table I). The reaction was carried out as follows. A 1.2 mol excess of NCS was added to a solution of 2 mmol of phenylthiocyclopropane(3) in 20 ml of benzene in the presence of a 1.5 mol excess of pyridine at room temperature. After keeping the mixture overnight at room temperature, the solution was poured into cold water and washed with 5% aqueous sodium thiosulfate, water, 5% aqueous hydrochloric acid, and water successively. The product(2) was purified further by distillation *in vacuo* (by bulb to bulb distillation).$^{9)}$

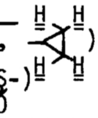
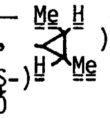
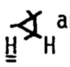
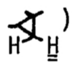
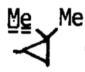
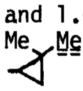
The chlorination of the sulfide with such chlorinating agents as NCS is generally considered to proceed via the initial formation of chlorosulfonium salt$^{11)}$ which then decomposes affording α-chlorosulfide. Thus, the reaction is considered to proceed via the ylide - ylene intermediate like in the Pummerer type reaction (see path B).

Preparation of 1-Chloro-1-(phenylsulfinyl)cyclopropanes(4a-c). Phenylsulfinylcyclo-

Table II. Preparation of 1-Chloro-1-(phenylsulfinyl)cyclopropanes(4a-c)



(1a-c) (4a-c)

Sulfoxides (1a-c)					Chlorinating Agents	Products(4a-c)					
	R_1	R_2	R_3	R_4			Yields (%)	Mp (°C)	IR Spectra (cm^{-1})(>S→O)	NMR Spectra (δ) ($CDCl_3$)	Analysis Found (Calcd.)
1a	H	H	H	H	$PhICl_2$	4a	92	50-51	1090, 1060	1.1-1.8(m,4H, ), 7.2-7.8(m,5H,Ph-$\underset{O}{S}$-)	C;54.10(53.86) H; 4.57(4.52) S;15.76(15.98)
1a	H	H	H	H	SO_2Cl_2	4a	85				
1b	Me	H	H	Me	$PhICl_2$	4b	87	76-77	1090, 1050	1.0-1.8(m,8H, ),7.3-7.8(m,5H,Ph-$\underset{O}{S}$-)	C;58.00(57.76) H; 5.77(5.73) S;14.22(14.02)
1c	Me	Me	H	H	$PhICl_2$	4c	86	76-77	1080, 1050	1.13 and 1.52(d,1H and d, 1H,  and ), 1.40 and 1.63(s,3H and s,3H,  and ), 7.3-7.8(m,5H,Ph-$\underset{O}{S}$-)	C;58.00(57.76) H; 5.73(5.73) S;13.78(14.02)

propanes(**1**) were treated with other chlorinating agents, i.e. iodobenzene dichloride or sulfuryl chloride, in the presence of pyridine and 1-chloro-1-(phenylsulfinyl)cyclopropanes(**4**) were obtained in good yields without ring opening (see Table II). The products(**4**), which were purified by column chromatography, were recrystallized further from ether - hexane. The structures of these products(4) were determined from their IR and NMR spectra. Although the chlorinating agents are quite different from those used in the previous cases, the reaction is also believed to proceed via chlorosulfoxonium salt as the intermediate.[7]

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7) The sulfoxides having a hydrogen atom on the α-carbon have been reported to react with such halogenating agents as NCS to afford the corresponding α-halosulfoxides; C. G. Venier and H. J. Barager, Org. Prepns. and Pro. Int., **6**, 77 (1974), and references cited therein.

8) Initially, 1-chloro-1-(phenylthio)cyclopropanes were prepared by treating (dichloromethylthio)benzene with potassium t-butoxide in various olefins by Schöllkopf et al.[2b]

9) In the reaction of these products, (**2a**) and (**2b**), with an equimolar amount of m-chloroperbenzoic acid in CH_2Cl_2 at 0°C for 5 h, the corresponding sulfoxides, (**4a**) and (**4b**), were obtained in yields of 78 and 72%, respectively. These compounds were identified by comparing their IR and NMR spectra with those of the samples obtained by the reaction of phenylsulfinylcyclopropanes, (**1a**) and (**1b**), with iodobenzene dichloride.

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