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The Preparation of *N*-(Alkylthio)- and *N*-(Arylthio)succinimides[1]

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N-(Organothio)succinimides have been known as useful starting materials for syntheses of various organic sulfur compounds and have previously been synthesized by the reactions of: (1) organic sulfides with *N*-bromosuccinimide (NBS),[2] (2) organic disulfides with NBS,[3] and with NBS in the presence of benzoyl peroxide[4] or pyridine,[5] and organic disulfides and trisulfides with *N*-chlorosuccinimide (NCS) in the presence of pyridine,[6] (3) sulfenyl halides with potassium succinimide[5] and with succinimide in the presence of triethylamine,[7] and (4) lead bisthiolates with NBS or NCS.[8] It has been reported that mercaptans react with NBS or NCS to give disulfides,[5] sulfenyl bromides, or chlorides.[9] In a benzene solution, thiophenol was reacted with NCS to give phenylsulfenyl chloride and succinimide at room temperature.[9]

However, we have found that an exactly equimolar mixture of mercaptans and NCS, after the addition of triethylamine, gives *N*-(organothio)succinimides. Aryl, aralkyl and alkyl mercaptans can give the corresponding *N*-(organothio)succinimides in good yields. The identification was performed by studying the IR spectra and by elemental analyses. Table 1 gives the various types of thiosuccinimides prepared by this method, together with the yields, melting points, and IR data.

The reaction of disulfide and trisulfide with NCS in the presence of pyridine as a catalyst was proposed by Hayashi to proceed by a radical mechanism which involved the cleavage of NCS to a succinimido radical and a chloro radical in the first step.[6] The present reaction between mercaptan and NCS would then seem to proceed through the initial formation of sulfenyl chloride by the electrophilic chlorination of mercaptan.[8] It follows that the sulfenyl chloride and succinimide produced simultaneously would be dehydrochlorinated by the addition of triethylamine, much as in the reaction of sulfenyl chloride and succinimide:[7]

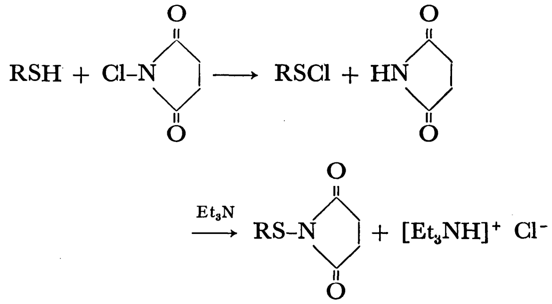
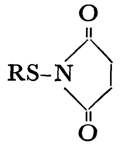


Table 1. The yields, mp, and IR spectra of the prepared *N*-(alkylthio)- and *N*-(arylthio)succinimides[a]



R	Yield (%)	Mp (°C)	(lit mp) (°C)	IR (C=O)[b] (cm^{-1})
Phenyl	78.2	117—117.5	(118—119)[5]	1740
o-Tolyl	71.2	88—88.5	(85.5—86)[2]	1730
m-Tolyl	86.4	108—109	(100—102)[7]	1725
p-Tolyl	75.6	114.5—115	(113.5)[2]	1725
p-Chlorophenyl	79.3	146—147	(142.5—143.5)[2]	1730
Benzyl	66.4	164—165	(165—166)[3]	1725
Benzhydryl	64.7	155—156		1725
Ethyl	34.2	48—49		1725
Isopropyl	68.6	48.5—49.5		1725
t-Butyl	79.6	156.5—157.5		1725
Cyclohexyl	74.5	106.5—107	(99)[7]	1725

a) Satisfactory elemental analyses were obtained for all compounds. Analytical data for the new compounds are shown in Experimental section.

b) All IR spectra were measured in KBr pellets.

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1) Chemistry of *N*-(Organothio)imides. III. For part II, see Y. Abe and J. Tsurugi, *Chemistry Lett.*, **1972**, 811.

2) W. Groebel, *Chem. Ber.*, **92**, 2887 (1959).

3) K. H. Büchel and A. Conte, *ibid.*, **100**, 1248 (1967).

4) W. Groebel, *ibid.*, **93**, 284 (1960).

5) H. Miyoshi and R. Oda, *Kogyo Kagaku Zasshi*, **59**, 224 (1956).

6) M. Furukawa, Y. Fujino, Y. Kojima, M. Ono, and S. Hayashi, *Chem. Pharm. Bull.* (Tokyo), **20**, 2024 (1972).

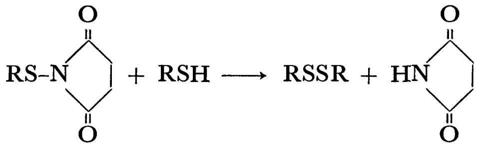
7) M. Behforouz and J. E. Kerwood, *J. Org. Chem.*, **34**, 51 (1969).

8) B. C. Pant and J. G. Noltes, *Inorg. Nucl. Chem. Lett.*, **7**, 63 (1971).

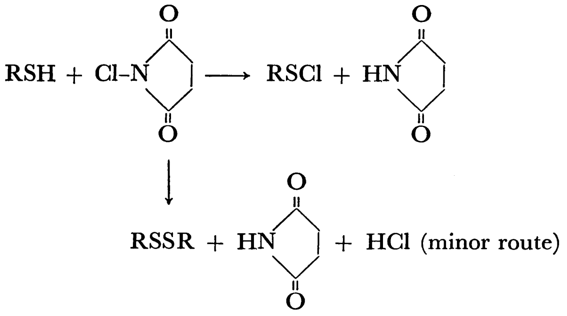
9) H. Emde, Ger, 804572 (1951); *Chem. Abstr.*, **46**, 529 (1952).

The red or orange coloration in the mixture solution of mercaptan, NCS, and benzene may be attributed to the formation of sulfenyl chloride. After the addition of triethylamine to this solution, the color of the reaction mixture fades. This indicates the consumption of sulfenyl chloride.

The use of an excess of mercaptan must be avoided. Otherwise, the product will be obtained in a lower yield than that shown in Table 1, because the *N*-(organothio)succinimide produced will react with the excess mercaptan to produce disulfide.[10,11]



Therefore, the purity of NCS must be determined by iodometrical titration and a calculated equimolar amount of NCS must be used. For example, in the case of the preparation of *N*-(phenylthio)succinimide, the yield increased from 55.1 to 78.2% as the NCS became more pure. The yield is still not quantitative, however. This may be because a part of the mercaptan is oxidized to disulfide by the reaction with NCS in spite of the major route to sulfenyl chloride. In fact disulfides were detected as by-products in all runs.



This method for the preparation of *N*-(organothio)-succinimide is superior to the method using chlorine gas[7] because the amount of NCS required as a chlorinating agent can be exactly and conveniently weighed, and it needs only one reaction vessel, even though the method involves two steps.

Experimental

All the melting points are uncorrected. The IR spectra were recorded with a JASCO IR-S spectrometer. The mercaptans were used without further purification. The purity of the NCS was determined by iodometrical titration before use.

General Procedure for the Preparation of N-*(Alkylthio)- and* N-*(Arylthio)succinimides.* A solution of mercaptan (20 mmol) in benzene (20 ml) at room temperature (*ca.* 20 °C) was added, all at once, to a suspension of NCS (20 mmol) in benzene (110 ml). After being stirred for 5 min, the mixture turned red or orange and the temperature rose to 30—35 °C. After the temperature had been depressed to 25 °C, a solution of triethylamine (21 mmol) in benzene (20 ml) was added, drop by drop, over a period of 5 min at 20—30 °C with cooling. The reaction mixture faded; it was then allowed to stand for 30 min, was washed thoroughly with water, and was then dried over anhydrous sodium sulfate. After the removal of the solvent, it was recrystallized from ethanol.

N-*(Benzhydrylthio)succinimide.* Found: C, 68.22; H, 5.02; N, 4.43; S, 10.52%. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71; S, 10.78%.

N-*(Ethylthio)succinimide.* Found: C, 45.33; H, 5.74; N, 8.75; S, 20.04%. Calcd for $C_6H_9NO_2S$: C, 45.27; H, 5.70; N, 8.80; S, 20.14%.

N-*(Isopropylthio)succinimide.* Found: C, 48.36; H, 6.48; N, 8.11; S, 18.72%. Calcd for $C_7H_{11}NO_2S$: C, 48.53; H, 6.40; N, 8.09; S, 18.51%.

N-*(*t-*Butylthio)succinimide.* Found: C, 51.39; H, 7.04; N, 7.45; S, 17.14%. Calcd for $C_8H_{13}NO_2S$: C, 51.31; H, 7.00; N, 7.48; S, 17.12%.

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[11] D. N. Harpp, D. K. Ash, T. G. Back, J. G. Greason, B. A. Orwig, W. H. VanHorn, and J. P. Snyder, *ibid.*, **1970**, 3551.