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THE REACTION OF SULFENIMIDES WITH TRIS(DIMETHYLAMINO)PHOSPHINE. A NOVEL SYNTHESIS OF AMINES AND THEIR PRECURSORS.[1]

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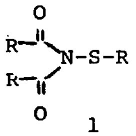
Although the sulfenimide grouping, 1, has been known for some



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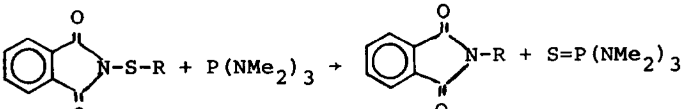
time[2], its chemistry has had very little study.

We wish to report a novel desulfurization reaction of sulfenimides which illustrates its potential as a synthetic intermediate. In addition, a phosphonium salt has been identified as an intermediate in the reaction. A variety of sulfenimides undergo facile desulfurization by tris(dimethylamino)phosphine (2)[3] to give N-substituted imides (3) (Table I) in excellent yield. Imides such as 3 are intermediates in the well-known Gabriel



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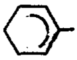
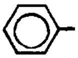
synthesis of amines[4]. On treatment of these compounds with KOH or, preferably, hydrazine, primary amines are produced in good yield. The Gabriel method of preparation appears to be limited to those primary alkyl amines where the carbon bearing the amine function is primary. In contrast, we have found that the desulfurization of N- isopropylthiophthalimide (8) affords a 77% yield of N- isopropylphthalimide. Conversion to the free amine with hydrazine was accomplished in 34% yield.

In general, this desulfurization procedure allows for the conversion of thio-systmes such as 4 to amines. The method thus provides an important alternative to the Gabriel reaction and may be particularly useful

$$\underset{\underline{4}\quad X= H,Cl,SR}{R\text{-}S\text{-}X} \rightarrow R\text{-}NH_2$$

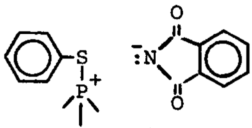
where the Gabriel procedure cannot be used.

TABLE I

SULFENIMIDE R	number	% N-Substituted phthalimide nmr	 isolation	% RNH$_2$
CH_3CH_2-	5	99	75	
$CH_3CH_2CH_2CH_2$-	6	99	46	
$C_6H_5CH_2$-	7	93	87	97[a]
$(CH_3)_2CH$-	8	95	77	34[d]
$(CH_3)_3C$-	9	b		
	10	b		
	11	c		
CH_3 	12	c		

a, yield by nmr; b, elimination occurs, phthalimide isolated in 80% yield; c, phosphonium salt formed; d, the volatility (bp 32°) of this compound, coupled with a small scale run made isolation difficult.

A typical experiment involves the addition of aminophosphine 2 to a benzene solution of the sulfenimide, both reactants in a 1:1 molar ratio. A rapid, exothermic reaction ensues which on chromatographic work-up or recrystallization provides the N-substituted phthalimides. Ethyl (5), n-butyl (6) and benzyl (7) sulfenimides were desulfurized in near quantitative yield (nmr). In addition, benzylamine was prepared in 97% yield (nmr) by treatment of 7 with hydrazine. Two aromatic sulfenimides[5], (R=phenyl(11), p-tolyl(12)), when treated with phosphine 2, gave no desulfurization. Instead, phosphonium salts 13 and 14 were formed as evidenced by an appropriate ^{31}P nmr signal for the phenyl derivative 13 (-59.1 ppm from H_3PO_4)[6] and the appearance of a



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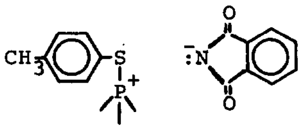

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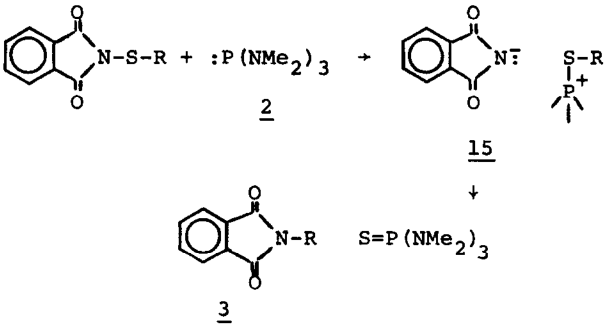
doublet (J=2 Hz) for the aromatic methyl group[7] in p-tolyl sulfenimide (14). In cases of t-butyl (9) and cyclohexyl (10) sulfenimides, the reaction with aminophosphine 2 effected desulfurization, but isobutylene and cyclohexene were formed along with substantial amounts of phthalimide.

These results can readily be accomodated by the following mechanism:



When R is hindered (cyclohexyl (10) or t-butyl (9)), elimination rather than substitution on the R group occurs at the phosphonium salt stage (15) resulting in phthalimide, the corresponding alkene, and tris(dimethylamino)phosphine sulfide. In the aromatic cases (R = phenyl, 11, and p-tolyl, 12), only the phosphonium salt was isolated since its decomposition to N- arylphthalimide and phosphine sulfide would require a nucleophilic displacement on the unactivated aromatic ring. Evidence for the phosphonium salt intermediate for the aliphatic members was obtained by treating the authentic phosphonium salt[8] 16 with potassium phthalimide. The only products observed were N-benzylphthalimide and phosphine sulfide.

$$(Et_2N)_3P^+\text{-}SCH_2C_6H_5$$

16 BF_4^-

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(2) M. Behforouz and J.E. Kerwood, *J. Org. Chem.*, **34**, 51(1969) and references cited therein.

(3) This phosphine desulfurizes a wide variety of organosulfur compounds: see D.N. Harpp, J.G. Gleason and J.P. Snyder, *J. Am. Chem. Soc.*, **90**, 4181(1968) and D.N. Harpp and J.G. Gleason, *Tetrahedron Letters* 1447(1969).

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(5) N-(Benzothiazole-2-thio)phthalimide was prepared (appropriate mass spectrum) but could not be purified. This impure material underwent desulfurization but purification of the N-(benzothiazole-2-)phthalimide was unsuccessful.

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(7) C.E. Griffen and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4427(1967).

(8) D.N. Harpp and J.G. Gleason, unpublished results.

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