Anal. Calcd for $C_{17}H_{10}N_4S$: C, 67.5; H, 3.3; N, 18.5. Found: C, 67.4; H, 3.3; N, 18.3.

A General Procedure for *N*-(2′-Cyanovinyl)methylphenylsulfilimines (36, 37).—A methanolic solution of 1 mmol of **5** was added to a methanolic solution of 1 mmol of the cyano olefins **30** or **31** and the reaction mixture was allowed to stand at room temperature for 30 min. The solvent was evaporated and the residue was purified by plc using $CHCl_3$ as solvent and recrystallization from benzene–ether.

***N*-(2′,2′-Dicyanovinyl)methylphenylsulfilimine (36)** was obtained from **5** and **30** in 96% yield as white plates: mp 149–150°; ir (KCl) 2150 (s), 1525 cm^{-1} (s); uv max (EtOH) 218 nm (sh, log ϵ 3.85), 292 (4.23); nmr ($CDCl_3$) τ 2.0 (1 H, s, olefinic proton), 2.1–2.6 (5 H, m, aromatic protons), 7.0 (3 H, s, CH_3); mass spectrum *m/e* (rel intensity) 215 (M^+, 12) 124 (100).

Anal. Calcd for $C_{11}H_9N_3S$: C, 61.4; H, 4.2; N, 19.5. Found: C, 61.15; H, 4.3; N, 19.4.

***N*-(2′-Cyano-2′-ethoxycarbonylvinyl)methylphenylsulfilimine (37)** was obtained from **5** and **31** in 71% yield as white needles: mp 117–118°; ir (KCl) 2180 (s), 1650 cm^{-1} (m); uv max (EtOH) 215 nm (sh, log ϵ 4.20), 296 (4.48); nmr ($CDCl_3$) τ 1.42 (1 H, s, olefinic proton), 2.1–2.6 (5 H, m, aromatic protons), 5.84 (2 H, q, J = 7 Hz, OCH_2CH_3), 6.95 (3 H, s, CH_3), 8.75 (3 H, t, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* (rel intensity) 262 (M^+, 2), 124 (100).

Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.5; H, 5.4; N, 10.7. Found: C, 59.7; H, 5.5; N, 10.4.

Reaction of 4 with 3-Ethoxymethylenepentane-2,4-dione (38). A solution of 1 mmol of **4** in 5 ml of $CHCl_3$ was added to a solution of 1 mmol of 3-ethoxymethylenepentane-2,4-dione (**38**)[25] in 5 ml of $CHCl_3$ and the reaction mixture was allowed to stand at room temperature for 10 min. The solvent was evaporated under reduced pressure and the residual oil was submitted to plc using benzene to give diphenyl sulfide (78%) and 4-acetyl-5-methylisoxazole (**40**)[18] (57%) as an oil. Replacing the solvent with methanol gave the similar result.

Reaction of 5 with 38.—Using a similar procedure described for the reaction of **4** with **38**, the reaction of **5** and **38** gave 3-aminomethylpentane-2,4-dione (**42**) in 78% yield, mp 145–145.5° (from benzene–methanol) (lit.[26] mp 142–144°), in addition to methyl phenyl sulfide.

Acknowledgment.—We thank Mr. Y. Kato of Hitachi Ltd. for determination of high-resolution mass spectra.

Registry No.—**1**, 36016-40-7; **2**, 39149-53-6; **3**, 39149-52-5; **4**, 36744-90-8; **5**, 42397-39-7; **6**, 39149-60-5; **7**, 42397-41-1; **8**, 39149-62-7; **9**, 42397-43-3; **10**, 42397-44-4; **11**, 42397-45-5; **12**, 70-34-8; **13**, 39149-63-8; **14**, 1087-09-8; **15**, 7338-94-5; **16**, 2632-15-2; **17**, 42397-48-8; **18**, 42397-49-9; **19**, 42397-50-2; **20**, 3672-49-9; **21**, 2039-49-8; **26**, 130-15-4; **27**, 2348-81-4; **28**, 941-69-5; **29**, 34314-68-6; **30**, 123-06-8; **31**, 94-05-3; **32**, 670-54-2; **33**, 42397-54-6; **34**, 42397-55-7; **35**, 42397-56-8; **36**, 42397-57-9; **37**, 42397-58-0; diphenyl sulfide, 139-66-2; methyl phenyl sulfide, 100-68-5; benzoyl chloride, 98-88-4; acetic anhydride, 108-24-7; ethyl chloroformate, 541-41-3; phenyl isocyanate, 103-71-9; ethyl 2-cyano-3-ethoxyacrylate, 94-05-3.

(25) L. Claisen, *Justus Liebigs Ann. Chem.*, **297**, 1 (1897).

(26) K. R. Huffman, F. C. Schaefer, and G. A. Peters, *J. Org. Chem.*, **27**, 551 (1962).

Synthesis and Properties of *N*-(Alkyl- and arylsulfinyl)phthalimides. A New Class of Sulfinyl-Transfer Reagents[1]

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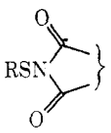
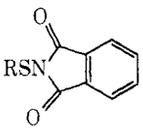
The synthesis and properties of *N*-(alkyl- and arylsulfinyl)phthalimides are described. These materials are converted in high yield to sulfinamides and sulfinate esters on treatment with amines and alcohols, respectively. The mass spectral behavior of the title compounds was also investigated in some detail.

The utility of thioimides **1** as sulfenyl-transfer reagents has been adequately demonstrated in the last few years.[2]



1



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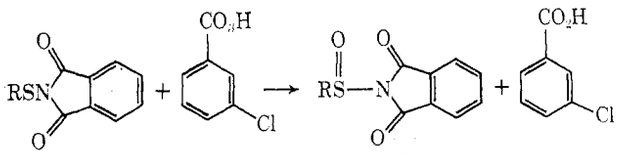
Recently we reported[3] that thiophthalimides **2** may be conveniently oxidized to the corresponding sulfinylphthalimides **3** with *m*-chloroperbenzoic acid.



2 3

Our continued investigation of sulfinylphthalimides has shown that these novel compounds possess extremely desirable properties as sulfinyl-transfer agents in much the same way as thioimides which transfer divalent sulfur. The title compounds are conveniently prepared in high yield from readily available thiophthalimides.[4] Furthermore, they are crystalline solids which are far more stable than comparable sulfinyl derivatives such as sulfinyl chlorides.[5] Also, sulfinylphthalimides react rapidly with nucleophiles, resulting in displacement of the phthalimide anion and formation of the corresponding sulfinyl derivative.

N-(Alkyl- and arylsulfinyl)phthalimides are prepared by the dropwise addition of 1 equiv of *m*-chloroper-

(1) Organic Sulfur Chemistry. XVII. For part XVI, see D. N. Harpp and T. G. Back, *Tetrahedron Lett.*, 5313 (1972).

(2) (a) K. S. Boustany and A. B. Sullivan, *Tetrahedron Lett.*, 3547 (1970); (b) D. N. Harpp, D. K. Ash, T. G. Back, J. G. Gleason, B. A. Orwig, W. F. VanHorn, and J. P. Snyder, *ibid.*, 3551 (1970); (c) D. N. Harpp and T. G. Back, *J. Org. Chem.*, **36**, 3828 (1971); (d) D. H. R. Barton, G. Page, and D. A. Widdowson, *Chem. Commun.*, 1466 (1970); (e) K. S. Boustany, *Chimia*, 396 (1970); (f) D. N. Harpp and T. G. Back, *Tetrahedron Lett.*, 4953 (1971); (g) Y. Abe and J. Tsurugi, *Chem. Lett.*, 441 (1972); (h) D. N. Harpp and T. G. Back, *Tetrahedron Lett.*, 1481 (1972); (i) T. Mukaiyama, S. Kobayashi, and T. Kumamoto, *ibid.*, 5115 (1970); (j) T. Mukaiyama and K. Saigo, *Bull. Chem. Soc. Jap.*, **44**, 3077 (1971); (k) T. Mukaiyama, S. Kobayashi, K. Kamio, and H. Takei, *Chem. Lett.*, 237 (1972).

(3) D. N. Harpp and T. G. Back, *Tetrahedron Lett.*, 5313 (1972).

(4) Thiophthalimides may be prepared in high yield from thiols or disulfides; see (a) M. Behforouz and J. E. Kerwood, *J. Org. Chem.*, **34**, 51 (1969); (b) K. H. Buchel and A. Conte, *Chem. Ber.*, **100**, 1248 (1967).

(5) I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **29**, 951 (1964).

benzoic acid to a cooled (0°) solution of the thiophthalimide in chloroform. When performed at room temperature, the reaction provides slightly lower yields. The desired compounds are easily separated from the by-product *m*-chlorobenzoic acid by trituration with ether, which dissolves the highly soluble acid but not the required product. After filtering, further purification is effected by recrystallization from chloroform–petroleum ether (bp 30–60°) or chloroform–ether. In the case of hindered sulfinylphthalimides, the *m*-chlorobenzoic acid is removed by washing the chloroform solution with 5% sodium bicarbonate. However, when bulky substituent groups are not present, this purification procedure results in rapid decomposition with formation of phthalimide. All sulfinylphthalimides produced are listed in Table I along with yields and physical data.

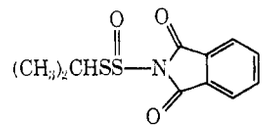
TABLE I

PREPARATION OF *N*-(ALKYL-, ARYL-, AND THIOSULFINYL)PHTHALIMIDES

Compd	R	Method[a,b]	Yield, %	Mp, °C
4	$C_6H_5CH_2$	B	96	154–155
5	CH_3	A	91	167–170
6	C_2H_5	A	85	132–134
7	*i*-C_3H_7	B	94	125–127
8	*n*-C_4H_9	A	80	87–88
9	*t*-C_4H_9	B	100	133–136
10	C_6H_5	A	89	150–153
11	*p*-$CH_3C_6H_4$	A	92	191–194
12	CH_3OCCH_2 (O above C)	A	87	135–136
13	*i*-C_3H_7S	A	87	93–94

[a] Method A, *m*-chlorobenzoic acid was removed by ether trituration; method B, acid was removed with 5% sodium bicarbonate solution. [b] In method A, significant second crops of product were sometimes obtained by cooling the ether filtrate.

In addition, isopropyl phthalimido disulfide[6] was similarly oxidized to the thiosulfinylphthalimide **13** in 87% yield.



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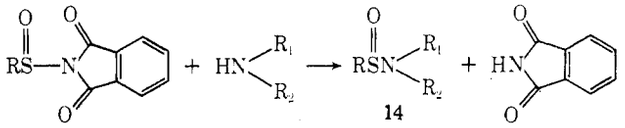
Evidence that oxidation occurs at the sulfur atom adjacent to the phthalimide group derives from nmr and mass spectral data (*vide infra*).

Preparation of Sulfinamides.—We have found that the aminolysis of sulfinylphthalimides provides a clean, rapid route for the synthesis of sulfinamides **14**. The latter compounds have traditionally been prepared by the reaction of sulfinyl chlorides with amines[7] or by the treatment of thionylamines with Grignard reagents.[8] Unfortunately, these methods often provide low yields owing to unstable precursors and concomitant side reactions. However, when sulfinylphthalimides react with primary or secondary amines in inert solvents such as carbon tetrachloride or benzene, high yields of the corresponding sulfinamides (**14**) are obtained.

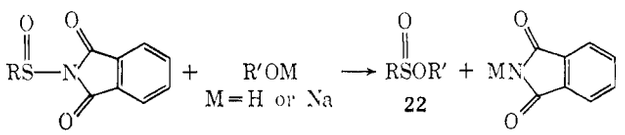


14

It is interesting to note that aniline, an aromatic amine, is sufficiently nucleophilic to generate sulfinanilide **21** in 88% yield. Filtration of phthalimide from the reaction mixture, followed by removal of the solvent *in vacuo*, provides the crude sulfinamide in quantitative yield. Traces of remaining phthalimide may be removed from the product by distillation or crystallization. The sulfinamides prepared by this method are listed in Table II.

Preparation of Sulfinate Esters.—The most frequently used method for preparing sulfinate esters **22** involves the alcoholysis of sulfinyl chlorides.[9] Aromatic sulfinate esters have also been prepared by the oxidation of disulfides or thiols with lead tetraacetate.[10] More recently, these compounds have been produced by the reaction of sodium sulfinates with chlorocarbonates in alcohols,[11] and by coupling sulfinic acids with alcohols using dicyclohexylcarbodiimide.[12] With the exception of the last method, these procedures all suffer from low yields and attendant side reactions.

We wish to report that sulfinylphthalimides are excellent precursors of sulfinate esters. They react with solutions of alkoxides in alcohols at room temperature to provide the products in high yield. Alternately, the alcoholysis may be accomplished by simply refluxing the sulfinylphthalimide in the appropriate alcohol. The latter method affords sulfinate esters in nearly quantitative yields and in a high state of purity.



22

In either procedure, the desired sulfinate esters are isolated by filtration of the insoluble material, evaporation of the alcohol *in vacuo*, and extraction of the product from the remaining residue with pentane. In the case of less soluble sulfinate esters (*e.g.*, **28**), it is advantageous to use 10% methylene chloride–pentane in the extraction step. The product obtained by removal of solvent under reduced pressure is generally pure as verified by tlc. Products are listed in Table III with yields and physical data.

An anomalous result was observed when *N*-(*tert*-butylsulfinyl)phthalimide (**9**) was treated with sodium isopropoxide solution. Rather than effecting displace-

(6) D. N. Harpp and D. K. Ash, *Int. J. Sulfur Chem., Part A*, **1**, 57 (1971).

(7) (a) L. C. Raiford and S. E. Hazlet, *J. Amer. Chem. Soc.*, **57**, 2172 (1935); (b) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 805 (1958).

(8) (a) H. Gilman and H. L. Morris, *J. Amer. Chem. Soc.*, **48**, 2399 (1926); (b) D. Klamann, C. Sass, and M. Zelenka, *Chem. Ber.*, **92**, 1910 (1959).

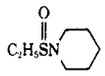
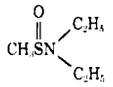
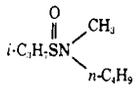
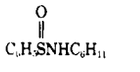
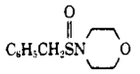
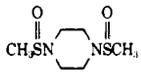
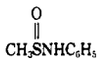
(9) (a) H. Phillips, *J. Chem. Soc.*, 2552 (1925); (b) I. B. Douglass, *J. Org. Chem.*, **30**, 633 (1965); (c) J. W. Wilt, R. G. Stein, and W. J. Wagner, *J. Org. Chem.*, **32**, 2097 (1967).

(10) L. Field, C. B. Hoelzel, and J. M. Locke, *J. Amer. Chem. Soc.*, **84**, 847 (1962).

(11) M. Kobayashi and M. Terao, *Bull. Chem. Soc. Jap.*, **39**, 1292 (1966).

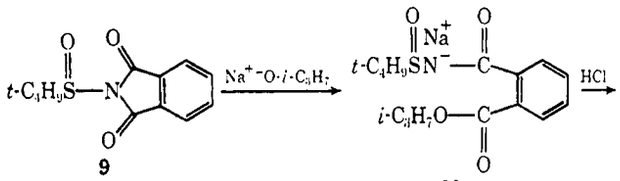
(12) Y. Miyaji, H. Minato, and M. Kobayashi, *Bull. Chem. Soc. Jap.*, **44**, 862 (1971).

TABLE II
PREPARATION OF SULFINAMIDES

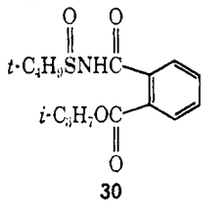
Compd	Sulfinamide	Yield, %	Solvent[a] (time, hr)	Mp or bp, °C (mm)	Lit. mp or bp, °C (mm)	n^{25}
15		77	CCl_4(1)	60–61 (0.1)		1.4964
16		80	CCl_4(1)	51–52 (0.9)	55 (1.8)[c]	1.4635
17		80	CCl_4(1)	56–57 (0.08)		1.4619
18		89	C_6H_6(0.5)[b]	114–115	116[d]	
19		94	C_6H_6(1)	83–85		
20		77	CCl_4(1)	149–154		
21		88	C_6H_6(12)	84–87	86–88[e]	

[a] Reaction of 19 was refluxed; all others were performed at room temperature. [b] The sulfinylphthalimide solution was added dropwise over 10 min to the amine solution. [c] Y. H. Chiang, J. S. Luloff, and E. Schipper, *J. Org. Chem.*, **34**, 2397 (1969). [d] Reference 8b. [e] Reference 7b.

ment of the phthalimide group, the alkoxide caused ring opening as depicted below.



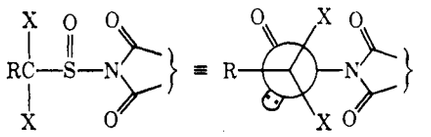
9 29



30

The sodium salt **29** was obtained in 90% yield and on acidification with HCl gave amide **30**. In addition to appropriate aliphatic signals, the latter compound showed a broad peak in the nmr spectrum at τ 1.9 (>NH) which was absent in product **29**. Furthermore, this peak disappeared on addition of D_2O. The identity of compound **30** was confirmed by a correct elemental analysis. It appears that, when the substituent group of the sulfinylphthalimide is bulky, the approaching alkoxide is diverted from the usual attack on sulfur to the less hindered carbonyl carbon atom. An analogous reaction might also explain the somewhat lower yield of sulfinate ester **25**, where isopropyl groups on both the nucleophile and the substrate create sufficient steric hindrance to allow some attack at carbon to take place. The reaction shown above is similar to the ring opening of thiophthalimides by certain primary amines.[2f,13]

Nmr Spectra of Sulfinylphthalimides, Sulfinamides, and Sulfinate Esters.—It has been well established that the sulfur atom of sulfinyl compounds constitutes a chiral center. As a result, geminal substituents in the proximity of a sulfinyl moiety possess a diastereotopic relationship which may manifest itself as observed nonequivalence in the nmr spectrum. Such effects have been previously reported in a variety of sulfinyl derivatives, including sulfoxides,[14] sulfinate esters,[15] sulfinamides,[16] and sulfinyl chlorides.[17] Our studies on the nmr spectra of sulfinylphthalimides have revealed that the three compounds shown below display complex spectra attributable to the presence of the sulfinyl group.



Compd	R	X
4	C_6H_5	H
7	H	CH_3
12	CH_3OC (O)	H

The methylene protons of the benzyl (**4**) and carbomethoxymethyl (**12**) derivatives exhibited AB quartets and the isopropyl group of product **7** showed nonequivalent methyl protons, as evidenced by the presence of two doublets in the spectrum. These doublets remained unchanged on heating to 100°. The α-methylene group in *N*-(*n*-butylsulfinyl)phthalimide (**8**) showed a crude triplet which might have shown further splitting with better resolution and the ethyl de-

(13) K. S. Boustany and J. P. VanderKooi, *Tetrahedron Lett.*, 4983 (1970).

(14) A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *J. Amer. Chem. Soc.*, **87**, 5498 (1965).

(15) (a) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961); (b) M. Oki and H. Iwamura, *Bull. Chem. Soc. Jap.*, **35**, 1428 (1962); (c) J. W. Wilt and W. J. Wagner, *Chem. Ind. (London)*, 1389 (1964).

(16) R. M. Moriarty, *J. Org. Chem.*, **30**, 600 (1965).

(17) G. Canalini and G. Maccagnani, *Tetrahedron Lett.*, 3035 (1971).

TABLE III
PREPARATION OF SULFINATE ESTERS

Compd	Sulfinate ester	Yield, %	Method[a] (time, hr)	Bp, °C (mm)	Lit. bp, °C (mm)	Refractive index
23	n-$C_4H_9S(O)OCH_3$	80	A (0.5)	84–85 (12)	72–73 (10)[h]	n^{23} 1.4430[e]
24	$C_6H_5S(O)OC_2H_5$	86	A (0.5)	56–57 (0.05)	58 (0.05)[i]	n^{23} 1.5315[f]
25	i-$C_3H_7S(O)$-i-C_3H_7	63	A (0.5)	58–59 (9)	*c*	n^{22} 1.4325
26	$C_6H_5S(O)OCH_3$	90	A (0.5)	*b*		n^{25} 1.5432[g]
		95	B (2)	43–44 (0.07)	47.5–51 (0.2)[j]	
27	$C_6H_5CH_2S(O)OC_2H_5$	97	B (3)	69–71 (0.025)		n^{22} 1.5362
28	$CH_3OC(O)CH_2S(O)OCH_3$	93	B (2)	59–61 (0.1)	*d*	n^{22} 1.4585

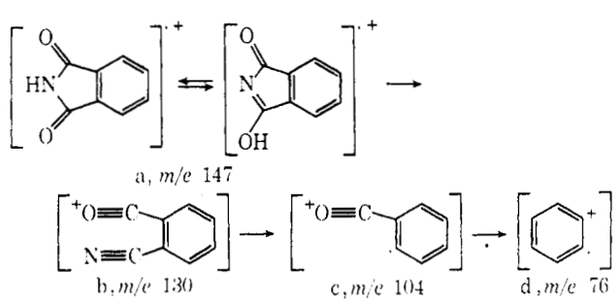
[a] Method A, the precursor was treated with alkoxide in alcohol at room temperature; method B, alcoholysis was achieved by refluxing with the alcohol. [b] The product had ir, nmr, and refractive index identical with those of samples prepared by method B and by the procedure of Douglass (ref 9b). [c] Only the nmr spectrum is reported in the literature: F. Seel, J. Bondier, and W. Gombler, *Chem. Ber.*, **102**, 443 (1969). [d] The preparation of this compound is reported in the literature but no physical data are furnished: D. O. DePree, U. S. Patent 3,014,069 (1958); *Chem. Abstr.*, **56**, 14085*b* (1962). [e] Lit.[9b] n^{25} 1.4438. [f] Lit. n^{20} 1.5308: J. Michalski, T. Modro, and J. Wieczorkowski, *J. Chem. Soc.*, 1665 (1960). [g] Lit.[9b] n^{25} 1.5437. [h] Reference 9b. [i] See Michalski, *et al.* (footnote *f*). [j] Reference 10.

rivative **6** displayed no splitting beyond a quartet for the geminal protons. Although complex spectra might be expected in the last two instances, their absence can be the result of negligible differences in the conformer populations and a low intrinsic diastereomerism.[18]

The nmr spectrum of *N*-[*S*-(isopropylthio)sulfinyl]-phthalimide (**13**) shows a single doublet attributable to the two methyl groups as well as a heptet from the methine proton at τ 6.6. The latter shift compares favorably with that of an isopropyl methine proton adjacent to divalent sulfur, but is considerably further upfield than that of a similar proton next to a sulfinyl moiety. For example, the chemical shifts of the methine protons in isopropyl phthalimido disulfide and in *N*-(isopropylsulfinyl)phthalimide are τ 6.7 and 5.5, respectively. These observations strongly support the proposed structure **13** in which the isopropyl group is adjacent to sulfenyl rather than sulfinyl sulfur.

None of the sulfinate esters in Table III show complex splitting arising from nonequivalent groups in the substituent attached to sulfur. The benzyl methylene group of **27** and the geminal protons of **28** both appear as singlets, while the methyl groups in the isopropyl moiety adjacent to sulfur in **25** display one doublet. On the other hand, groups attached to oxygen often show further splitting. For example, the methylene group of ester **24** provides a 16-line spectrum[15a] while the methyl hydrogens of the isopropyl group adjacent to oxygen in sulfinate ester **25** display two doublets revealing their diastereotopic nature. The ethyl methylene group of ester **27**, however, shows only a quartet. The nmr spectra of all other compounds listed in Tables I–III are consistent with their structures.

Mass Spectra of Sulfinylphthalimides.—Since mass spectral studies of sulfinyl compounds have rarely been reported in the literature,[19] we felt it instructive to study the electron-impact fragmentations of sulfinylphthalimides (Table IV). We observed that all products in Table I display parent peaks varying in relative intensity from <1% in the isopropyl, *n*-butyl, and *tert*-butyl derivatives (**7**, **8**, **9**) to 29% in the methyl analog **5**. All sulfinylphthalimides also show intense peaks at *m/e* 147, 130, 104, and 76 likely arising from fragments a–d. The loss of CO from c is also manifested by a metastable peak at *m/e* 55.5.



The occurrence of fragments a–d has also been reported in the mass spectra of thiophthalimides[2c,20] and alkyl phthalimido disulfides.[6]

Cleavage of the C–S bond in sulfinylphthalimides with the charge remaining on either the carbon or the

(18) M. Raban, *Tetrahedron Lett.*, 3105 (1966). It is interesting to note that, when the phthalimide moiety of sulfinylphthalimide **4** was replaced by morpholine to give sulfinamide **19**, the AB pattern of the former was observed as a singlet which remained unsplit in a variety of solvents and on cooling to −45°. Similarly, it has been reported that the methylene protons of benzylsulfinyl chloride appear as a singlet, a fact attributed by the authors to conformational equilibria and low intrinsic asymmetry.[17]

(19) (a) J. Ø. Madsen, C. Nolde, S. O. Lawesson, G. Schroll, J. H. Bowie, and D. H. Williams, *Tetrahedron Lett.*, 4377 (1965); (b) J. H. Bowie, F. C. V. Larsson, G. Schroll, S. O. Lawesson, and R. G. Cooks, *Tetrahedron*, **23**, 3743 (1967); (c) W. H. Baarschers and B. W. Krupay, *Can. J. Chem.*, **51**, 156 (1973); (d) S. Kozuka, H. Takahashi, and S. Oae, *Bull. Chem. Soc. Jap.*, **43**, 129 (1970). A detailed description of the fragmentation of sulfinamides and sulfinate esters will be reported separately.

(20) B. A. Orwig, M.S. Thesis, McGill University, 1970.

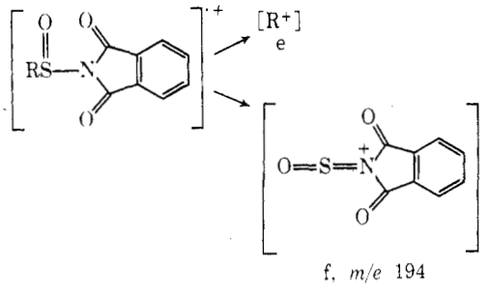
TABLE IV

MASS SPECTRA OF N-(ALKYL-, ARYL-, AND THIOSULFINYL)PHTHALIMIDES (3)[a]

		Rel intensities								
Compd	R	P+	a	b	c	d	e	f	g	h	i
4	$C_6H_5CH_2$	3	90	<1	55	58	100	8			
5	CH_3	29	16	20	18	27	6	36			
6	C_2H_5	6	15	100	29	41	19		19		
7	i-C_3H_7	<1	10	100	13	18	23		66		
8	n-C_4H_9	<1	88	92	100	88	50		42		
9	t-C_4H_9	<1	9	33	15	27	100		27		
10	C_6H_5	14	100	26	58	60	42	8		46	7
11	p-$CH_3C_6H_4$	14	100	3	57	52	34	<1		29	8
12	$CH_3O_2CCH_2$	10	100	5	78	68		37			2
13	i-C_3H_7S	2	80	38	100	96			10		

[a] Other major peaks (>10%), *m/e* (rel intensity): **4**, 148 (11), 110 (16), 103 (16), 92 (11), 83 (13), 78 (11), 77 (18), 74 (11), 66 (13), 65 (16), 51 (13), 50 (29); **5**, 160 ($P^+ - SOH$, 36), 148 (14), 63 (10), 50 (16), 46 (CH_2S, 100); **6**, 174 ($P^+ - SOH$, 17), 148 (12), 131 (10), 105 (15), 103 (15), 90 (12), 50 (19), 46 (CH_2S, 37); **7**, 46 (11), 41 (15); **8**, 149 (13), 148 (27), 131 (12), 106 (15), 105 (15), 103 (27), 90 (15), 81 (19), 77 (15), 75 (19), 74 (19), 69 (18), 63 (23), 59 (12), 56 (26), 55 (42), 50 (46), 46 (CH_2S, 23), 44 (23), 43 (92), 41 (77); **9**, 50 (15), 46 (15), 41 (45); **10**, 148 (11), 109 (18), 103 (14), 97 (12), 78 (22), 75 (11), 74 (13), 66 (18), 65 (12), 51 (36), 50 (34), 44 (16); **11**, 148 (11), 124 (15), 103 (14), 91 (34), 77 (11), 65 (11), 58 (11), 50 (25), 44 (23), 43 (25), 40 (62); **12**, 148 (17), 103 (20), 92 (13), 90 (12), 79 (18), 75 (15), 74 (13), 50 (35), 46 (52), 45 (22); **13**, 179 ($C_8H_5NO_2S$, 56), 178 (17), 151 (11), 148 (12), 105 (49), 103 (28), 91 (11), 77 (14), 75 (19), 74 (14), 50 (44), 46 (14), 41 (64).

sulfur-containing fragment is also observed. All compounds in Table I except **12** show intense peaks corresponding to the alkyl or aryl fragment e where charge is retained on the carbon atom. When this cation is exceptionally stable, it constitutes the base peak of the spectrum as in the case of the benzyl and *tert*-butyl derivatives **4** and **9**. Alternately, it is possible for the charge to reside on the sulfur-containing fragment. Hence benzyl-, methyl-, phenyl-, and carbomethoxymethylsulfinylphthalimides (**4**, **5**, **10**, and **12**, respectively) display a strong peak at *m/e* 194, attributed to fragment f. This process is confirmed by a metastable peak for the last compound only.

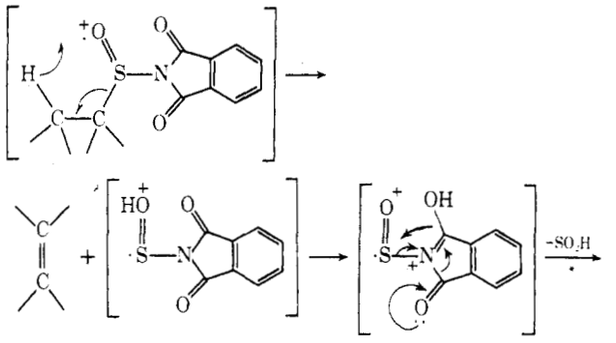


f, *m/e* 194

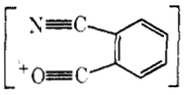
When hydrogen atoms are available β to the sulfinyl group, the fragmentation is altered. Instead of f, a strong ion is observed at *m/e* 195, suggesting a five-center McLafferty-type rearrangement[21] involving formation of g with elimination of alkene as depicted below. This transformation is observed in ethyl-, isopropyl-, *n*-butyl-, and *tert*-butylsulfinylphthalimides (**6**–**9**) and is accompanied by the corresponding metastable peak for compound **7**. Loss of SO_2H as a neutral fragment from g then results in formation of b.

(21) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967, p 123.

The appearance of a metastable ion at *m/e* 86.7 for compounds **6**–**9** confirms this process.



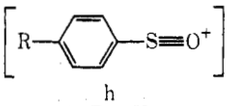
g, *m/e* 195



b

It thus appears that rupture of the C–S bond is a prominent feature in sulfinylphthalimide fragmentation resulting in abundant ions corresponding to e as well as either f or g depending on whether or not β hydrogens are present.

In addition, arylsulfinylphthalimides **10** and **11** produce strong ions at *m/e* 125 and 139, respectively, suggesting formation of fragment h.

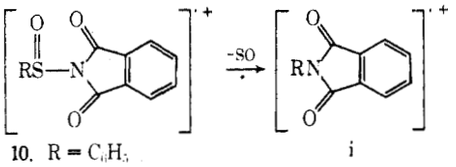


h

10, R = H

11, R = CH_3

Derivatives **10**, **11**, and **12** lose SO directly from the molecular ion to produce i; the corresponding metastable ions are found at *m/e* 183.5, 197.1, and 179.6, respectively. Similar behavior has been previously reported in the case of sulfoxides.[19a]



10, R = C_6H_5

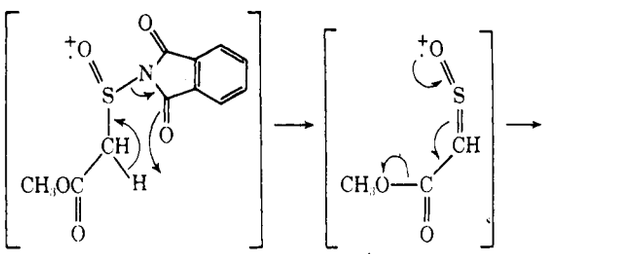
11, R = p-$CH_3C_6H_4$

12, R = CH_3OCCH_2 (‖ O)

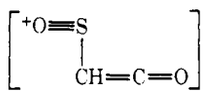
i

The mass spectrum of sulfinylphthalimide **12** is somewhat anomalous by virtue of abundant ions at *m/e* 120 and 89. These are best rationalized by loss of phthalimide from the molecular ion to generate j, followed by loss of $\cdot OCH_3$ giving the moiety k.

The fragmentation of the thiosulfinylphthalimide **13** resembles that of alkyl- and arylsulfinylphthalimides by the presence of intense peaks at *m/e* 147, 130, 104, 76, and 195, due to formation of a–d and g, respectively. The existence of the latter ion in the mass spectrum of **13** provides further evidence for the proposed site of oxidation during its preparation. It would be unlikely for such a fragment to be produced were not the sulfinyl group adjacent to the phthalimide

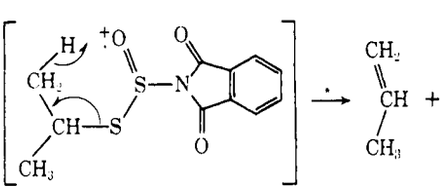


m/e 267 j, m/e 120

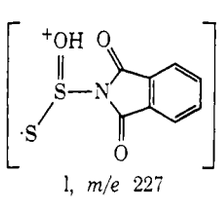


k, m/e 89

nitrogen. In addition, a strong ion at m/e 43 suggests formation of the isopropyl cation. Furthermore, loss of propene from the molecular ion is indicated by a large peak at m/e 227 (70%) and is confirmed by the presence of a metastable ion at m/e 191.6. This transformation is illustrated below.



m/e 269



l, m/e 227

Stability of Sulfinylphthalimides.—Sulfinylphthalimides **4–10** were stored in screw-top vials at room temperature with no noticeable decomposition over several weeks. After 2 months the methyl, ethyl, phenyl, and *n*-butyl derivatives showed signs of decomposition as evidenced by discoloration and lowered melting points. Less severe decomposition occurred in the benzyl and isopropyl analogs, while the *tert*-butyl compound was observed to remain unchanged. Shelf life may be prolonged considerably by storing the products at lower temperatures.

The title compounds appear to decompose rapidly in basic media to furnish phthalimide and presumably the corresponding sulfinic acid. When *N*-(*p*-tolylsulfinyl)phthalimide (**12**) was stirred with 5% sodium carbonate solution for 1.5 hr at room temperature, phthalimide was recovered in 84% yield. Stability toward base appears to be enhanced by the presence of bulky substituents. For example, it has already been mentioned that chloroform solutions of hindered sulfinylphthalimides are sufficiently stable in base to permit washing with 5% sodium bicarbonate solution.

It appears that sulfinylphthalimides are less labile in acid. When the *p*-tolyl derivative was stirred in 10% hydrochloric acid for 0.5 hr at room temperature, no decomposition whatsoever occurred and the sulfinylphthalimide was recovered unchanged in 97% yield.

Experimental Section

All melting points were obtained on a Gallenkamp block and are uncorrected. Mass spectra were obtained by Mr. W. Budd on a Model AEI-MS-902 spectrometer. High- and low-temperature nmr spectra were recorded on a Varian Model HA-100 spectrometer by Mr. R. Simenon, while a Varian Model T-60 furnished all other spectra. Elemental analyses were obtained on a Hewlett-Packard Model 185 automatic C, H, N analyzer, or alternately were performed by Organic Microanalyses (Montreal). All new compounds gave satisfactory analytical results (C, H, N) except sulfinamide **17**, which was 0.5% low in carbon.

Preparation of *N*-(Alkyl-, aryl-, and thiosulfinyl)phthalimides (4–13).—All products listed in Table I were obtained by either of two fundamental procedures. Hence, only one example of each will be described in detail.

***N*-(Ethylsulfinyl)phthalimide (6). Method A.**—A solution of 2.03 g (10 mmol) of *m*-chloroperbenzoic acid (85%) in 20 ml of chloroform was added dropwise over 0.5 hr to a solution of 2.07 g (10 mmol) of *N*-(ethylthio)phthalimide in 40 ml of chloroform at 0–5°. Stirring and cooling were continued for 0.5 hr, after which solvent was evaporated *in vacuo*. The resulting white solid was triturated with 30 ml of ether and stirred vigorously for 5–10 min. The suspended solid was then filtered and washed with cold ether to give 1.90 g (85%) of the desired product, mp 130–131°. Recrystallization from chloroform–petroleum ether gave an analytical sample, mp 132–134°.

***N*-(*tert*-Butylsulfinyl)phthalimide (9). Method B.**—The peracid (85%, 5 mmol) in 10 ml of chloroform was added to the thiophthalimide (5 mmol) in 20 ml of chloroform in the same manner as described in method A. After stirring and cooling for 1 hr, the solution was washed with 3 × 20 ml of 5% sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure provided 1.26 g of product (quantitative), mp 130–131°. Recrystallization from chloroform–petroleum ether furnished an analytical sample, mp 133–136°.

Preparation of Sulfinamides 15–21.—A typical procedure involves the synthesis of *N*,*N*-diethylmethylsulfinamide (**16**) and is described below. All other sulfinamides were obtained in an analogous manner.

A solution containing 1.05 g (5 mmol) of *N*-(methylsulfinyl)-phthalimide and 0.37 g (5 mmol) of diethylamine in 20 ml of carbon tetrachloride was stirred for 1 hr at room temperature. Insoluble material was then filtered to give 0.67 g (91%) of phthalimide, mp 228–231° (lit.[22] mp 238°). Evaporation of solvent from the filtrate furnished 0.70 g (104%) of the crude product as a clear oil. Distillation gave 0.54 g (80%) of the pure sulfinamide, bp 51–52° (0.9 mm) [lit.[23] bp 55° (1.8 mm)].

Preparation of Sulfinate Esters 23–28.—All compounds in Table III were produced by one of two basic procedures.

Methyl Phenyl Sulfinate (26). Method A.—To a solution of 0.14 g (2.5 mmol) of sodium methoxide in 10 ml of methanol was added 0.68 g (2.5 mmol) of *N*-(phenylsulfinyl)phthalimide. After 0.5 hr of stirring at room temperature, the methanol was evaporated *in vacuo*. The residue was then stirred vigorously with 15 ml of pentane which was subsequently decanted. The pentane extraction was repeated several more times and the washings were combined and evaporated under reduced pressure; the resulting clear oil weighed 0.35 g (90%). Purity of this product was confirmed by its homogeneity on tlc [silica gel; benzene–ethyl acetate (5:1)]. Furthermore, the product had ir and nmr spectra as well as refractive index identical with those of genuine samples prepared by method B as well as by the method of Douglass.[9b]

Method B.—The *N*-(phenylsulfinyl)phthalimide (0.81 g, 3 mmol) was refluxed in 5 ml of methanol. The solution became clear and several minutes later a precipitate formed. After 2 hr the reaction mixture was cooled, 0.33 g of phthalimide was filtered, mp 232–236°, and the methanol was evaporated from the filtrate *in vacuo*. Extraction of the product with pentane was performed as a method A, leaving behind a residue of 0.11 g of phthalimide (total yield of phthalimide 0.44 g, quantitative). Evaporation of pentane under reduced pressure provided 0.45 g (95%) of the product as a clear oil which was homogeneous on tlc, bp 43–44° (0.07 mm) [lit.[10] bp 47.5–51° (0.2 mm)].

Preparation of *N*-(*tert*-Butylsulfinyl)phthalic Acid Monoamide Isopropyl Ester (30).—To 10 ml of a 0.25 *M* solution of sodium

(22) "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Co., Cleveland, Ohio.

(23) Y. H. Chiang, J. S. Luloff, and E. Schipper, *J. Org. Chem.*, **34**, 2397 (1969).

isopropoxide in isopropyl alcohol was added 0.63 g (2.5 mmol) of *N*-(*tert*-butylsulfinyl)phthalimide. After 0.5 hr of stirring at room temperature, the isopropyl alcohol was evaporated *in vacuo*. The resulting solid foam was taken up in 40 ml of pentane and precipitation of a white solid occurred on cooling. Filtration gave 0.75 g (90%) of the sodium salt **29**, mp 159° dec.

A portion of this material (0.33 g, 1 mmol) was then dissolved in 5 ml of water and acidified to Congo Red end point with hydrochloric acid. The resulting precipitate was filtered and washed with water to furnish 0.25 g (80% of theoretical yield based on the sodium salt **29**) of the amide **30**, mp 115–116°. The product was recrystallized from chloroform–petroleum ether to provide an analytical sample of unchanged melting point.

Acknowledgment.—We thank the National Research Council of Canada and the Defense Research Board of Canada (Grant No. 9530-97) for financial support of this work.

Registry No.—**2** (R = $C_6H_5CH_2$), 14204-26-3; **2** (R = CH_3), 40167-20-2; **2** (R = C_2H_5), 17796-70-2; **2** (R = *i*-C_3H_7), 17796-72-4; **2** (R = *n*-C_4H_9), 17796-73-5; **2** (R = *t*-C_4H_9), 17796-75-7; **2** (R = C_6H_5), 14204-27-4; **2** (R = *p*-$CH_3C_6H_4$), 15199-26-5; **2** (R = $CH_3O_2CCH_2$), 42300-49-2; **2** (R = *i*-C_3H_7S), 33704-40-4; **4**, 40167-14-4; **5**, 40167-13-3; **6**, 40167-12-2; **7**, 40739-92-2; **8**, 40318-14-7; **9**, 40167-16-6; **10**, 40167-15-5; **11**, 42300-58-3; **12**, 42300-59-4; **13**, 42300-60-7; **15**, 42300-61-8; **16**, 921-77-7; **17**, 42300-63-0; **18**, 35810-04-9; **19**, 40167-17-7; **20**, 42300-66-3; **21**, 42300-67-4; **23**, 673-80-3; **24**, 1859-03-6; **25**, 22598-57-8; **26**, 670-98-4; **27**, 42300-72-1; **28**, 42300-73-2; **29**, 42300-74-3; **30**, 42300-75-4; piperidine, 110-89-4; diethylamine, 109-89-7; *N*-methylbutylamine, 110-68-9; cyclohexylamine, 108-91-8; morpholine, 110-91-8; piperazine, 110-85-0.

Reaction of 4-Substituted Pyridines with Sulfenyl Chlorides[1]

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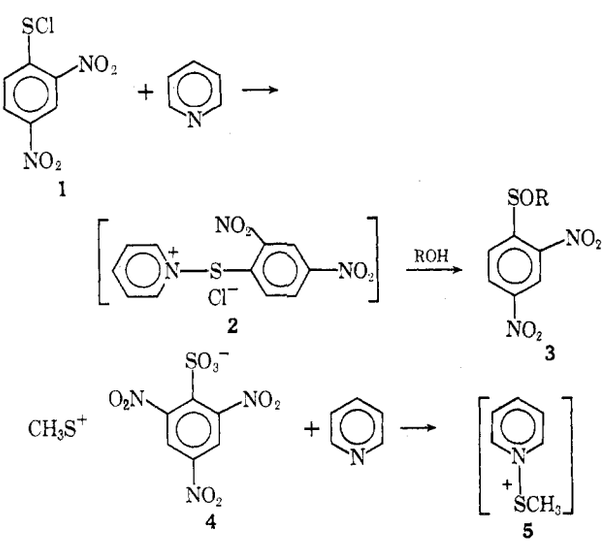
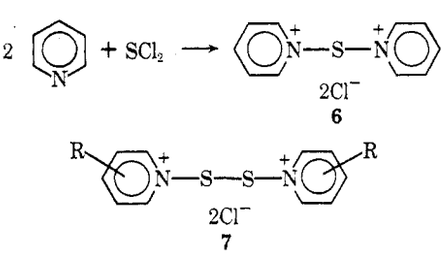
The reaction of 4-alkylpyridines with two substituents on the side-chain α carbon and arylsulfenyl chlorides gave α,α-disubstituted 4-pyridylmethyl aryl sulfides in 48–95% yield. When trichloromethanesulfenyl chloride and 4-benzhydryl- or 4-isopropylpyridine were allowed to react, diphenyl-4-pyridylmethyl or 2-(4-pyridyl)-2-propyl chloride were formed in 99 and 95% yield, respectively, while reaction of these 4-alkylpyridines with sulfur monochloride gave diphenyl-4-pyridylmethyl disulfide (~66%) or 2-(4-pyridyl)-2-propyl disulfide (82%). Analogous 3-alkyl- and 2-alkylpyridines failed to react with any of the above sulfenyl chlorides. A proposed rationalization of these reaction products entails formation of thiopyridinium ions and follows a pathway similar to the rearrangement of 4-alkylpyridine *N*-oxides and acid anhydrides.

The formation of *N*-arylthiopyridinium salts has been proposed by Kharasch[3] to explain pyridine catalysis in the conversion of 2,4-dinitrobenzenesulfenyl chloride (**1**) and alcohols to sulfenate esters **3**; however, attempts to isolate **2** were unsuccessful. More recently,



Helmkamp and coworkers[4] implied the formation of the *N*-methylthiopyridinium cation (**5**) when pyridine was added to a solution of **4** in nitrobenzene or nitromethane. The nmr upfield shift of the SCH_3 resonance supported structure **5** but no salt was isolated. However, crystalline *N*-thiopyridinium salts of structure **6** and **7** have been obtained from the reaction of pyridine



and sulfur dichloride[5] or sulfur monochloride.[6,7] In expanding our interest from *N*-oxypyridinium salts[8,9] to *N*-thiopyridinium salts we have investigated the reaction of various sulfenyl chlorides with a number of alkylpyridines and describe the results in this paper.

When a 2:1 molar solution of 4-benzhydrylpyridine (**15**) and 2,4-dinitrobenzenesulfenyl chloride (**1**), respectively, in dry ethylene chloride was stirred at room temperature for 1 hr, the reaction mixture gave a 48% yield of diphenyl-4-pyridylmethyl 2,4-dinitrophenyl sulfide (**16**) and a 38% yield of 2,4-dinitrophenyl disulfide (**9**). This reaction had been extended to other

(1) Presented in part before the Organic Division at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(2) Abstracted from a portion of the Ph.D. Dissertation submitted by J. N. R. in April 1973 at West Virginia University.

(3) L. Goodman and N. Kharasch, *J. Amer. Chem. Soc.*, **77**, 6541 (1955).

(4) G. K. Helmkamp, D. C. Owsley, W. M. Barnes, and H. N. Cassey, *J. Amer. Chem. Soc.*, **90**, 1635 (1968).

(5) U. Wannagat and G. Schindler, *Angew. Chem.*, **69**, 784 (1957).

(6) H. G. Heal and J. Kane, *J. Inorg. Nucl. Chem.*, **29**, 1539 (1967).

(7) R. C. Paul, K. Kishore, D. Singh, and K. C. Malhotra, *Indian J. Chem.*, **8**, 829 (1970).

(8) V. J. Traynelis and A. I. Gallagher, *J. Org. Chem.*, **35**, 2792 (1970).

(9) V. J. Traynelis in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1969, p 1.