Reactions of N-Unsubstituted Arylsulfilimines with Acylating Agents and with Activated Halobenzenes, Alkynes, and Alkenes

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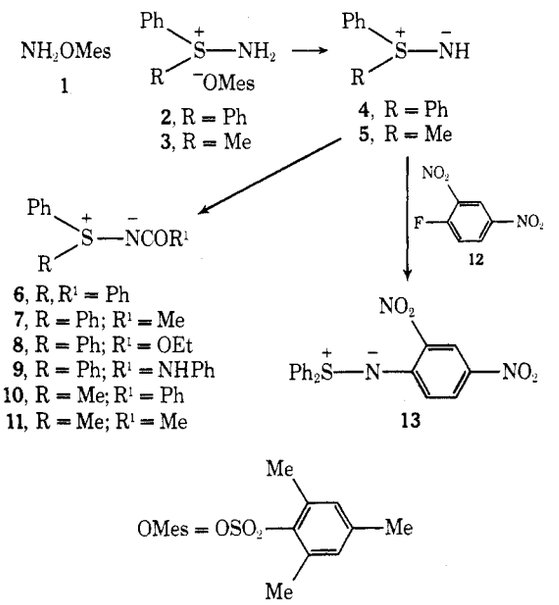
The arylsulfilimines (**4** and **5**) exhibit typical nucleophilicity in that they could be readily acylated with acylating agents and undergo substitution reactions with 2,4-dinitrofluorobenzene and Michael-type addition reactions with activated alkynes and alkenes under very mild conditions.

The previously investigated reactions of N-unsubstituted sulfilimines include oxidation,[1,2] hydrolysis,[1-3] thermolysis,[1-3] N-tosylation,[1-4] and reaction with carbon dioxide and carbon disulfide.[1] As our contribution to this relatively unexplored area, we have examined the nucleophilic reactions of the N-unsubstituted sulfilimine with acylating agents, 2,4-dinitrohalobenzenes, and some activated alkynes and alkenes. The present work was undertaken in part to explore the synthetic potential of sulfilimines, particularly as aminating reagents. It was also of interest to compare the physical and chemical properties of sulfilimines with those of other ylides such as sulfoximines and pyridinium *N*-imines. We chose diphenylsulfilimine (**4**) and methylphenylsulfilimine (**5**), which were conveniently synthesized by reaction of the corresponding sulfides with *O*-mesitylenesulfonylhydroxylamine (**1**) followed by anion exchange or base treatment.[4,5]

Reactions with Acylating Agents.—A simple and general method for N-acylation of sulfilimines is now reported. This procedure could be used as a route to the otherwise unavailable *N*-acylsulfilimines, for example, *N*-acylarylsulfilimines.[6] Thus, an ethanolic solution of arylsulfilimines (**4** and **5**) prepared by passing a solution of *S*-aminoarylsulfonium mesitylenesulfonates (**2** and **3**) in ethanol through anion exchange resin, was treated with acylating agents such as benzoyl chloride, acetic anhydride, ethyl chloroformate, or phenyl isocyanate to give the corresponding *N*-acylsulfilimines (**6**–**11**) in good to high yields (Scheme I).

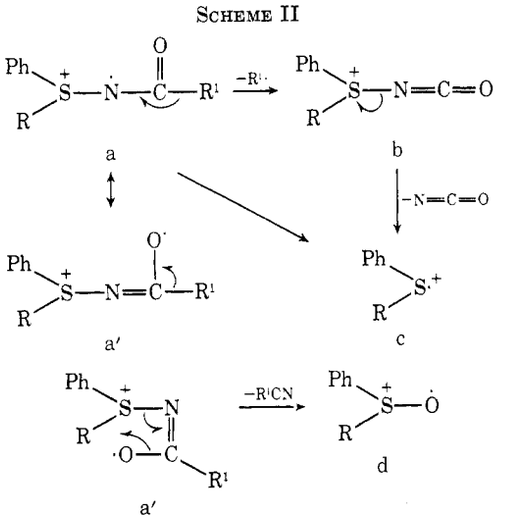
These *N*-acylsulfilimines showed ir carbonyl absorption bands characteristic of the betaine structures,[6-8] and uv absorption maxima at 217–231 nm, which were not affected by the nature of the acyl substituents, with the one exception of a phenylcarbamoyl group. Of particular interest is that the mass spectral behavior of *N*-acylarylsulfilimines (**6**–**11**) closely resembles that of *N*-acyliminopyridinium betaines.[9] Thus, the primary fragmentation process is α cleavage of the molecular

SCHEME I



ion a or a′ to give an ion b at *m/e* 228 (R = Ph) or 166 (R = Me). This ion b decomposes further by elimination of NCO to furnish a sulfide ion radical c at *m/e* 186 (R = Ph) or 124 (R = Me). The ion c may also be directly derived from the molecular ion by S–N bond fission. The other prominent peak observed in the upper mass range of *N*-benzoyl and *N*-acetyl derivatives (**6**, **7**, **10**, and **11**) is a sulfoxide ion d, which probably arises *via* a four-membered transition state (Scheme II).

SCHEME II



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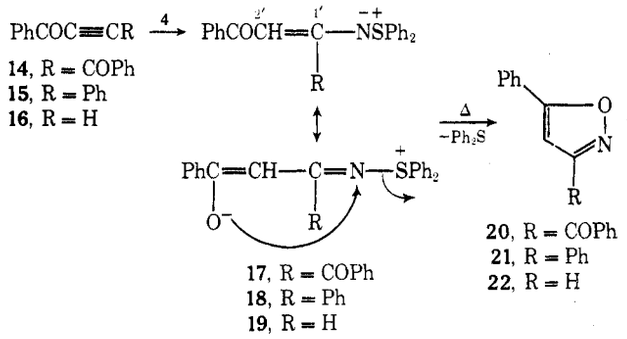
Reactions with 2,4-Dinitrohalobenzenes.—Under conditions similar to those employed for acylation, diphenylsulfilimine (**4**) failed to react with 2,4-dinitrochlorobenzene, but reacted readily with 2,4-dinitrofluorobenzene (**12**) to give *N*-(2 4-dinitrophenyl)diphenylsulfilimine (**13**) in 89% yield. This result suggests that **4** is a weaker nucleophile than pyridinium *N*-imine which undergoes a substitution reaction with 2,4-dinitrochlorobenzene.[10]

Reactions with Benzoylacetylenes.—Ylides such as sulfoxonium methylides[11] or sulfoximines[12] are known to undergo Michael addition reactions with acetylenic compounds. Diphenylsulfilimine (**4**) has now been shown to behave similarly to give 1:1 adducts. For example, when dibenzoylacetylene (**14**) was treated with **4** in chloroform at room temperature, the mixture immediately developed a yellow color. The nmr spectrum of the reaction mixture, monitored in $CDCl_3$, indicated that the reaction was complete in a few minutes. The adduct **17** was isolated as yellow crystals in 90% yield. In the same manner, benzoylphenylacetylene (**15**) or benzoylacetylene (**16**) each gave 1:1 adducts, **18** and **19**, in 68% yield (Scheme III).

SCHEME III

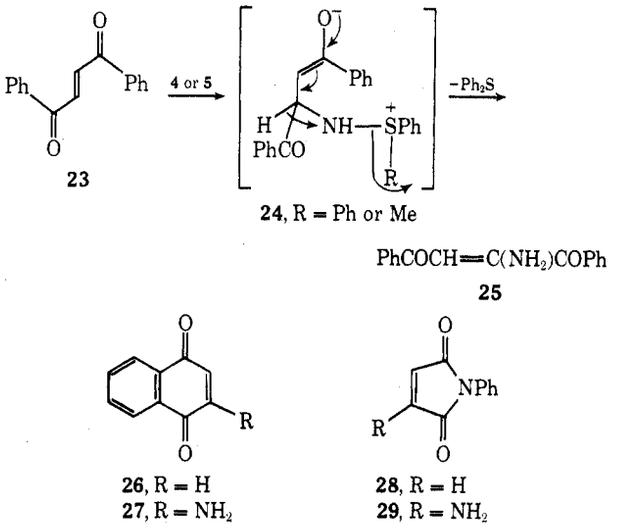


The structures of these adducts (**17–19**) were assigned on the basis of spectral data. For example, the adduct **19** exhibited two uv absorption maxima at 229 and 357 nm and has no carbonyl absorption bands above 1610 cm^{-1}, indicating that the carbonyl group is polarized. The nmr spectrum showed an AB type quartet at τ 3.6 (disappeared on treatment with D_2O) and 1.4 with a coupling constant of 13 Hz, which were assigned to $C_{2'}$ and $C_{1'}$ protons, respectively.

Confirmation of the structures of the adducts was provided by converting them into the corresponding known isoxazoles (**20–22**) in good yields by refluxing in chloroform for 1 hr. An analogous reaction is the transformation of 3-azidovinyl ketones into isoxazoles.[13]

Reactions with *trans*-1,2-Dibenzoylethylene, 1,4-Naphthoquinone, and *N*-Phenylmaleimide.—Treatment of **4** with *trans*-1,2-dibenzoylethylene (**23**) in chloroform at room temperature gave 1-amino-1,2-dibenzoylethylene (**25**) in 53% yield (Scheme IV). Similarly 1,4-naphthoquinone (**26**) and *N*-phenylmaleimide (**28**) gave the amine derivatives **27** and **29**, in 79 and 83% yields, respectively. Methylphenylsulfilimine (**5**) was also found to react with **23** in methanol to give the same product (**25**) in 90% yield. The formation of these amines (*e.g.*, **25**) presumably proceeds *via* initial addition of the sulfilimine **4** to the olefins (*e.g.*, **23**) giving an intermediate (*e.g.*, **24**), which undergoes a hydride shift to the nitrogen atom with concomitant S–N bond cleavage.

SCHEME IV



A formally analogous reaction has been reported by Sasaki and coworkers with *N*-ethoxycarbonyliminopyridinium betaine in the presence of acid.[14]

In contrast to the reaction of **4** with **23**, **26**, and **28**, the less activated olefins such as chalcone, benzylideneacetone, methyl vinyl ketone, or maleic anhydride failed to react with **4** even under refluxing conditions in chloroform; only unchanged starting material was recovered.

Reactions with Ethoxymethylene Derivatives of Malononitrile, Ethyl Cyanoacetate, Acetylacetone, and Tetracyanoethylene.—Diphenylsulfilimine (**4**) was observed to react readily with ethoxymethylene derivatives of malononitrile (**30**), ethyl cyanoacetate (**31**), and tetracyanoethylene (**32**) in chloroform at room temperature to give new stabilized diphenylsulfilimine derivatives (**33–35**) in high yields (Scheme V). Methylphenylsulfilimine (**5**) behaved analogously when a methanolic solution of **5** was treated with **30** and **31** to give the corresponding methylphenylsulfilimine derivatives (**36** and **37**). The structures of these products were evident on the basis of the elemental analyses and spectral evidence, the details of which are given in the Experimental Section. These reactions of the sulfilimines are analogous to those of the other ylides such as phosphonium ylides,[15] sulfoxonium ylides,[16] pyridinium ylides,[17] and pyridinium *N*-imines[18] and can be

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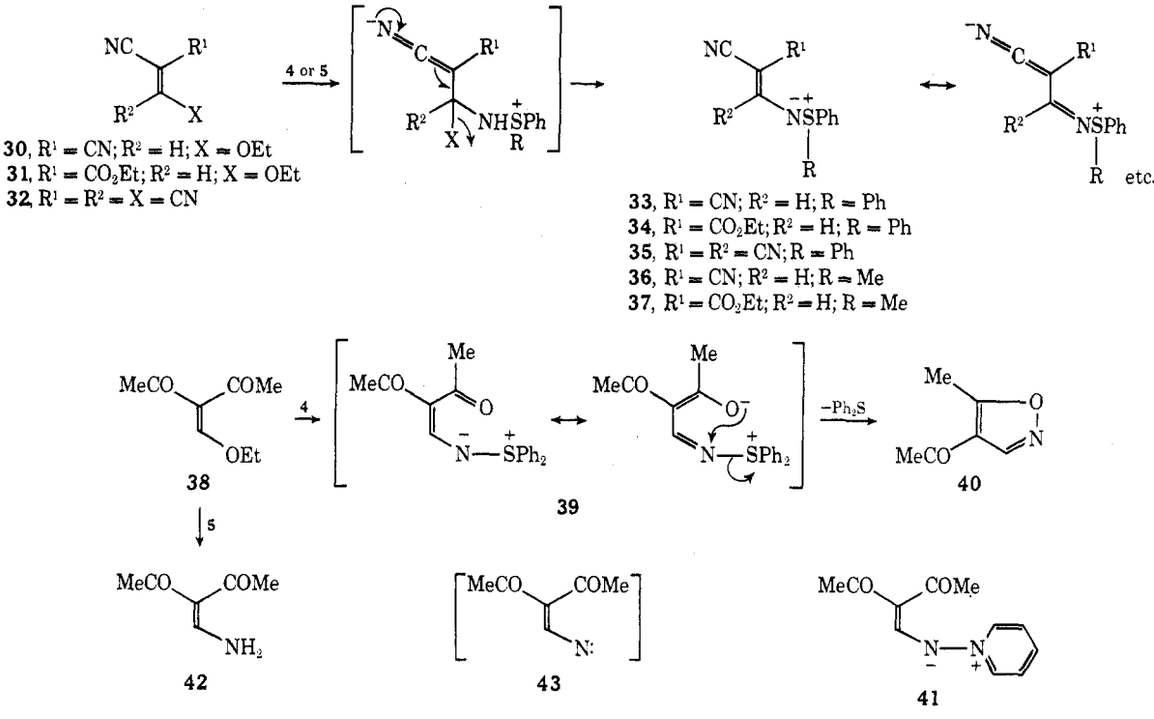
SCHEME V



envisaged as proceeding by an addition–elimination mechanism.[19]

By contrast, similar treatment of **4** with 3-ethoxymethylenepentane-2,4-dione (**38**) in either chloroform or methanol gave the known 4-acetyl-5-methylisoxazole (**40**) and diphenyl sulfide. Since the related *N*-(2′,2′-diacetylvinylimino)pyridinium betaine (**41**)[18] has also been shown to undergo similar thermal reaction to form **40**, it may be assumed that the species **39** is an intermediate. This can undergo ring closure in concert with elimination of diphenyl sulfide to lead to the observed product **40**. On the other hand, when methylphenylsulfilimine (**5**) was treated with **38**, 3-aminomethylenepentane-2,4-dione (**42**) was obtained as the sole product in 78% yield. Although this is formally the product of hydrogen abstraction by a possible vinylnitrene (**43**) from solvent, we have at present no evidence to support the nitrene intermediate.

The greater stability of the cyanovinyl substituted sulfilimines (**33–37**) may be attributed to the enhanced charge distribution over the nitrile group.[20]

Experimental Section

Melting points are uncorrected. Nmr spectra were determined with a Hitachi R-20A spectrometer (tetramethylsilane as internal standard). Ir spectra were recorded with a Hitachi EPI-G2 spectrophotometer, and uv spectra with a Hitachi 124 spectrophotometer. Low- and high-resolution mass spectra were obtained with Hitachi RMU-6D and RMU-7M instruments, respectively, with a direct inlet system operating at 70 eV. Preparative layer chromatography (plc) was carried out on Merck alumina PF_{254}.

Diphenylsulfilimine (4). A.—A solution of 430 mg (2 mmol) of *O*-mesitylenesulfonylhydroxylamine (**1**, MSH) in 2 ml of CH_2Cl_2 was added to a solution of 372 mg (2 mmol) of diphenyl sulfide in 2 ml of CH_2Cl_2 with ice cooling. The reaction mixture was allowed to stand at room temperature for 30 min. After addition of ether, the precipitate was recrystallized from CH_2Cl_2–ether to give 720 mg (90%) of *S*-aminodiphenylsulfonium mesitylenesulfonate (**2**), mp 119–120°.

Anal. Calcd for $C_{21}H_{23}NO_3S_2$: C, 62.8; H, 5.8; N, 3.5. Found: C, 62.7; H, 5.8; N, 3.6.

A solution of the salt in methanol or ethanol was passed through a column of Amberlite IRA-410 ion-exchange resin (strong base, OH^- form) to give an alcoholic solution of **4**. Evaporation of the solvent under reduced pressure gave a white solid in quantitative yield, which was recrystallized from benzene–*n*-hexane (*ca.* 5:2): mp 69–71° (as the monohydrate) (lit.[3] mp 70°); uv max (EtOH) 226 nm (sh, log ε 4.11).

B.—A solution of 21.5 g (0.1 mol) of MSH (**1**) in 100 ml of CH_2Cl_2 was added to a solution of 18.6 g (0.1 mol) of diphenyl sulfide in 100 ml of CH_2Cl_2 dropwise with ice cooling. After standing at room temperature for 1 hr, 50 ml of 20% NaOH solution was added to the reaction mixture. The precipitated white solid was filtered off, and the organic layer was washed with water and dried over $MgSO_4$. The dried extract was concentrated to give 39.2 g (88%) of **4** which was recrystallized from benzene–*n*-hexane (*ca.* 5:2).

Methylphenylsulfilimine (5).—Using a similar procedure to that described in method A, *S*-aminomethylphenylsulfonium mesitylenesulfonate (**3**) was prepared from methyl phenyl sulfide and **1** in 72% yield, mp 110–111°.

Anal. Calcd for $C_{16}H_{21}NO_3S_2$: C, 56.6; H, 6.2; N, 4.1. Found: C, 56.3; H, 6.2; N, 4.3.

Treatment of **3** with ion-exchange resin gave an alcoholic solution of **5**, which was used for the further reaction, uv max (EtOH) 214 nm (sh).

General Procedure for Acylation.—An ethanolic solution of **4** or **5** prepared by treatment of 1 mmol of **2** or **3** with ion-exchange resin was added to a solution of 1 mmol of benzoyl chloride, acetic anhydride, ethyl chloroformate, or phenyl isocyanate in 3 ml of ether with stirring at room temperature. After being stirred for 1–2 hr, the reaction mixture was concentrated and the residue was purified by chromatography on alumina using $CHCl_3$ as solvent or recrystallization.

***N*-Benzoyldiphenylsulfilimine (6)** was obtained from **4** and benzoyl chloride in 77% yield: mp 124–125° (from EtOH–ether); ir (KCl) 1595 (s), 1550 (s), 1330 cm^{-1} (s); uv max (EtOH) 231 nm (log ε 4.31), 254 (4.06); mass spectrum *m/e* (rel intensity) 305 (M^+, $C_{19}H_{15}NOS$, 3), 228 ($C_{13}H_{10}NOS$, b, 4), 212 ($C_{13}H_{10}NS$, 39), 202 ($C_{12}H_{10}OS$, d, 17), 186 ($C_{12}H_{10}S$, c, 63), 109 (C_6H_5S, 100), 105 (C_7H_5O, 35).

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Anal. Calcd for $C_{19}H_{15}NOS$: C, 74.7; H, 4.95; N, 4.6. Found: C, 74.7; H, 5.0; N, 4.5.

N-**Acetyldiphenylsulfilimine** (7) was obtained from **4** and acetic anhydride in 95% yield: mp 86–87° (from ether–AcOEt); ir (KCl) 1570 cm^{-1} (s); uv max (EtOH) 226 nm (sh, log ϵ 4.23); mass spectrum *m/e* (rel intensity) 243 (M^+, $C_{14}H_{13}NOS$ 3), 228 ($C_{13}H_{10}NOS$, b, 9), 204 ($C_{12}H_{12}OS$, 2), 202 ($C_{12}H_{10}OS$, d, 26), 186 ($C_{12}H_{11}S$, c, 100), 109 (C_6H_5S, 81).

Anal. Calcd for $C_{14}H_{13}NOS$: C, 69.1; H, 5.4; N, 5.8. Found: C, 69.1; H, 5.4; N, 5.7.

N-**Ethoxycarbonyldiphenylsulfilimine** (8) was obtained from **4** and ethyl chloroformate in 44% yield: mp 88.5–89° (from EtOH–ether); ir (KCl) 1610 cm^{-1} (s); uv max (EtOH) 226 nm (sh, log ϵ 4.13); mass spectrum *m/e* (rel intensity) 273 (M^+, $C_{15}H_{15}NO_2S$, 8), 228 ($C_{13}H_{10}NOS$, b, 12), 200 ($C_{12}H_{10}NS$, 9), 186 ($C_{12}H_{10}S$, c, 100).

Anal. Calcd for $C_{15}H_{15}NO_2S$: C 65.9; H, 5.5; N, 5.1. Found: C, 66.0; H, 5.4; N, 5.3.

N-(**Phenylcarbamoyl**)**diphenylsulfilimine** (9) was obtained from **4** and phenyl isocyanate in 83% yield: mp 133.5–135° (from AcOEt–*n*-hexane); ir (KCl) 3320 (m), 1610 cm^{-1} (s); uv max (EtOH) 242 nm (log ϵ 4.33); mass spectrum *m/e* (rel intensity) 320 (M^+, 4), 228 (b, 64), 200 (7), 186 (c, 100).

Anal. Calcd for $C_{19}H_{16}N_2OS$: C, 71.2; H, 5.0; N, 8.75. Found: C, 71.1; H, 5.1; N, 8.7.

N-**Benzoylmethylphenylsulfilimine** (10) was obtained from **5** and benzoyl chloride in 58% yield: mp 104.5–105° (from EtOH–ether); ir (KCl) 1590 cm^{-1} (s); uv max (EtOH) 229 nm (log ϵ 4.11), 253 (3.99); mass spectrum *m/e* (rel intensity) 243 (M^+, 2.2), 166 (b, 23), 150 (88), 140 (d, 63), 124 (c, 85), 109 (25), 105 (100).

Anal. Calcd for $C_{14}H_{13}NOS$: C, 69.1; H, 5.4; N, 5.8. Found: C, 69.3; H, 5.5; N, 5.8.

N-**Acetylmethylphenylsulfilimine** (11) was obtained from **5** and acetic anhydride in 91% yield as an oil: ir (KCl) 1570 cm^{-1} (s); uv max (EtOH) 217 nm (sh, log ϵ 4.16); mass spectrum *m/e* (rel intensity) 181 (M^+, 2), 166 (b, 28), 140 (d, 63), 124 (c, 100), 109 (20); picrate mp 156–157.5° (from EtOH).

Anal. Calcd for $C_{15}H_{14}N_4O_8S$: C, 43.9; H, 3.4; N, 13.65. Found: C, 43.7; H, 3.5; N, 13.6.

N-(**2,4-Dinitrophenyl**)**diphenylsulfilimine** (13).—To an ethanolic solution of 220 mg of **4** was added 186 mg of 2,4-dinitrofluorobenzene (12). The reaction mixture was stirred at room temperature for 10 min and passed through a column of Amberlite IRA-410 ion-exchange resin. Evaporation of the solvent under reduced pressure gave 327 mg (89%) of a yellow solid of **13** which was recrystallized from benzene–EtOH: mp 133.5–134°; mass spectrum *m/e* (rel intensity) 367 (M^+, 2), 186 (100).

Anal. Calcd for $C_{18}H_{13}N_3O_4S$: C, 58.85; H, 3.6; N, 11.4. Found: C, 58.8; H, 3.5; N, 11.5.

N-(**1′,2′-Dibenzoylvinyl**)**diphenylsulfilimine** (17).—A solution of 41 mg of **4** in 1 ml of $CHCl_3$ was added to a solution of 43 mg of dibenzoylacetylene (14) in 1 ml of $CHCl_3$. After 5 min at room temperature, the solvent was evaporated to give 77 mg (90%) of yellow crystals, which were recrystallized from benzene: mp 131–133°; ir (KCl) 1670 (s), 1610 cm^{-1} (m); uv max (EtOH) 248 nm (log ϵ 4.13), 358 (3.96); nmr ($CDCl_3$) 1.85–2.95 (20 H, aromatic protons), 3.67 (1 H, s, olefinic proton); mass spectrum *m/e* (rel intensity), no M^+, 249 (3), 186 (47), 105 (100).

Anal. Calcd for $C_{28}H_{21}NO_2S$: C, 77.2; H, 4.9; N, 3.2. Found: C, 76.9; H, 4.8; N, 3.35.

N-(**2′-Benzoyl-1′-phenylvinyl**)**diphenylsulfilimine** (18).—Using a procedure similar to that described for **17**, this compound was obtained from 110 mg of **4** and 103 mg of benzoylphenylacetylene (15) in 68% yield as hygroscopic yellow needles: mp 119–122° (from benzene); ir (KCl) 1595 cm^{-1} (m); uv max (EtOH) 248 nm (sh, log ϵ 4.37), 380 (4.11); olefinic proton signal overlaps the aromatic proton multiplets; mass spectrum *m/e* (rel intensity) 407 (M^+, 1), 221 (36), 186 (100).

Anal. Calcd for $C_{27}H_{21}NOS$: C, 79.55; H, 5.2; N, 3.4. Found: C, 79.05; H, 5.15; N, 3.4.

N-(**2′-Benzoylvinyl**)**diphenylsulfilimine** (19).—Using a procedure similar to that described for **17**, this compound was obtained from 219 mg of **4** and 130 mg of benzoylacetylene (16) in 68% yield after purification by plc using $CHCl_3$ as a yellow oil which rapidly turned brown: ir (KCl) 1605 cm^{-1} (m); uv max (EtOH) 230, 357 nm. Satisfactory elemental analysis was not obtained owing to instability.

Thermal Reaction of *N*-(**1′,2′-Dibenzoylvinyl**)**diphenylsulfilimine** (17).—A solution of 44 mg of **17** in 3 ml of $CHCl_3$ was refluxed for 1 hr until the starting material disappeared on tlc. After evaporation of the solvent, the residual oil was submitted to plc using benzene as solvent to give 18.7 mg (75%) of 3-benzoyl-5-phenylisoxazole (20) [mp 81–82° (lit.[18] mp 80–82°); ir (KCl) 1650 (s), 1595 (m), 1570 (m), 1445 cm^{-1} (s)] in addition to diphenyl sulfide (98%).

Thermal Reaction of *N*-(**2′-Benzoyl-1′-phenylvinyl**)**diphenylsulfilimine** (18).—Treatment of **18** as described above gave diphenyl sulfide (64%) and 3,5-diphenylisoxazole (21, 54%): mp 142–143° (lit.[18] mp 141–143°); ir (KCl) 1610 (m), 1590 (m), 1570 (m), 1485 (m), 1445 cm^{-1} (s).

Thermal Reaction of *N*-(**2′-Benzoylvinyl**)**diphenylsulfilimine** (19).—Treatment of **19** as described above gave diphenyl sulfide (87%) and 5 phenylisoxazole (72%) as an oil which was identified by uv, ir, and nmr spectra.

1-Amino-1,2-dibenzoylethylene (25).—A solution of 219 mg of **4** in 3 ml of $CHCl_3$ was added to a solution of 230 mg of *trans*-1,2-dibenzoylethylene (23) in 3 ml of $CHCl_3$. The reaction mixture was allowed to stand for 30 min at room temperature. Evaporation of the solvent under reduced pressure gave a mixture of two products, which were separated by plc using benzene–cyclohexane as solvent to give diphenyl sulfide (87%) and 1-amino-1,2-dibenzoylethylene (25, 53%), mp 136–137° (lit.[21] mp 137.5–138.5°). Replacing the solvent with methanol gave **25** in 90% yield.

2-Amino-1,4-naphthoquinone (27).—Mixing 219 mg of **4** and 158 mg of 1,4-naphthoquinone (26) in 3 ml of $CHCl_3$ gave a red colored solution, from which red crystals precipitated. After 30 min, the crystals were collected and recrystallized from benzene to give red needles of 2-amino-1,4-naphthoquinone (27) in 79% yield: mp 205–208° (lit.[22] mp 207°); ir (KCl) 3370 (m), 3200 (m), 1680 (m), 1615 (s), 1560 cm^{-1} (s).

2-Amino-*N***-phenylmaleimide** (29).—In a way similar to that described for **25**, 2-amino-*N*-phenylmaleimide (29) was obtained from 219 mg of **4** and 173 mg of *N*-phenylmaleimide (28) in 82% yield: mp 108° (from benzene); ir ($CHCl_3$) 3490 (m), 3380 (m), 1715 (s), 1655 cm^{-1} (s); uv max (EtOH) 233 nm (log ϵ 4.31), 258 (4.03), 360 (3.45); nmr ($CDCl_3$) τ 2.50–3.00 (5 H, m, aromatic protons), 4.70–5.00 (2 H, NH_2), 4.90 (1 H, s, olefinic proton).

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.8; H, 4.3; N, 14.9. Found: C, 63.9; H, 4.4; N, 14.6.

General Procedure for *N*-(**2′-Cyanovinyl**)**diphenylsulfilimines** (**33–35**).—A solution of 1 mmol of **4** in 3 ml of $CHCl_3$ was added to a solution of 1 mmol of the cyano olefins **30–32** in 2 ml of $CHCl_3$ and the reaction mixture was allowed to stand at room temperature for 10 min. The solvent was evaporated and the product was purified by plc using $CHCl_3$ as solvent and recrystallization from $CHCl_3$–petroleum ether (bp 30–60°).

N-(**2,2′-Dicyanovinyl**)**diphenylsulfilimine** (33) was obtained from **4** and ethoxymethylenemalononitrile[23] (30) in 40% yield as white needles: mp 129–131°; ir (KCl) 2150 (s), 1520 cm^{-1} (s); uv max (EtOH) 230 nm (sh, log ϵ 4.10), 295 (4.35); nmr ($CDCl_3$) τ 1.85 (1 H, s, olefinic proton), 2.20–2.60 (10 H, m, aromatic protons); mass spectrum *m/e* (rel intensity) 277 (M^+, 1), 186 (100).

Anal. Calcd for $C_{16}H_{11}N_3S$: C, 69.3; H, 4.0; N, 15.15. Found: C, 69.5; H, 4.1; N, 14.8.

N-(**2′-Cyano-2′-ethoxycarbonylvinyl**)**diphenylsulfilimine** (34) was obtained from **4** and ethyl 2-cyano-3-ethoxyacrylate[24] in 71% yield as white needles: mp 169–172°; ir (KCl) 2200 (s), 1680 cm^{-1} (m); uv max (EtOH) 230 nm (sh, log ϵ 4.16), 300 (4.46); nmr ($CDCl_3$) τ 1.30 (1 H, s, olefinic proton), 2.1–2.6 (10 H, m, aromatic protons), 5.79 (2 H, q, J = 7 Hz, OCH_2CH_3), 8.70 (3 H, t, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* (rel intensity) 324 (M^+, 1), 186 (69), 171 (100).

Anal. Calcd for $C_{18}H_{16}N_2O_2S$: C, 66.7; H, 5.0; N, 8.6. Found: C, 66.7; H, 5.2; N, 8.4.

N-(**1′,2′,2′-Tricyanovinyl**)**diphenylsulfilimine** (35) was obtained from **4** and tetracyanoethylene (32) in 87% yield as yellow needles: mp 139–140°; ir (KCl) 2200 cm^{-1} (s); uv max (EtOH) 240 nm (sh, log ϵ 4.01), 342 (4.27); nmr ($CDCl_3$) τ 2.0–2.6 (m, aromatic protons); mass spectrum *m/e* (rel intensity) 302 (M^+, 3), 186 (100).

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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.

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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.

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

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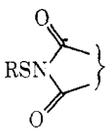
The synthesis and properties of *N*-(alkyl- and arylsulfinyl)phthalimides are described. These materials are converted in high yield to sulfinamides and sulfinate esters on treatment with amines and alcohols, respectively. The mass spectral behavior of the title compounds was also investigated in some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

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



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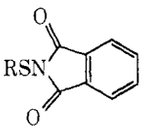

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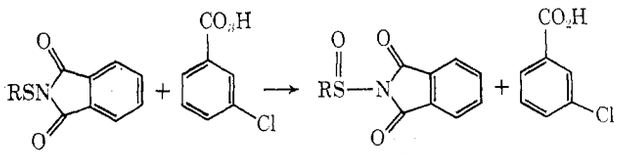
Recently we reported[3] that thiophthalimides **2** may be conveniently oxidized to the corresponding sulfinylphthalimides **3** with *m*-chloroperbenzoic acid.



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-

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