Reaction of *S,S*-Diphenylsulfilimine with Aldehydes; A New Synthesis of Nitriles

Yvonne Gelas-Mialhe, Roger Vessière*

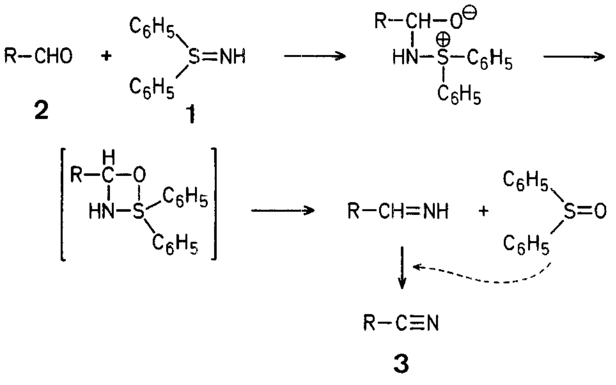
Groupe de recherche de Chimie Organique 2, Université de Clermont-Ferrand, B.P. 45, F-63170 Aubiere, France; and Ecole Nationale Supérieure de Chimie, 71 Boulevard Côte-Blatin, F-63000 Clermond-Ferrand, France

Nucleophilic addition reactions of sulfilimines with α,β-unsaturated carbonyl compounds have been reported; two types of products are isolated, after elimination of sulfides: aziridines and enamines[1-5]. In these reactions, sulfilimines behave like sulfur-carbon ylids. Nucleophilic properties of sulfilimines have also been shown by the reaction of *N*-methyldiphenylsulfilimine with phenyl isocyanate[6]. The isolation of triphenylsulfilimine from this reaction may be rationalized to occur via a four-center intermediate reminiscent of the Wittig reaction[6]. However, unlike sulfur-carbon ylids or phosphorus-carbon ylids, *N*-methyl-*S,S*-diphenylsulfilimine failed to react with the carbonyl group of ketones[4,6].

0039-7881/80/1232-1005 $ 03.00

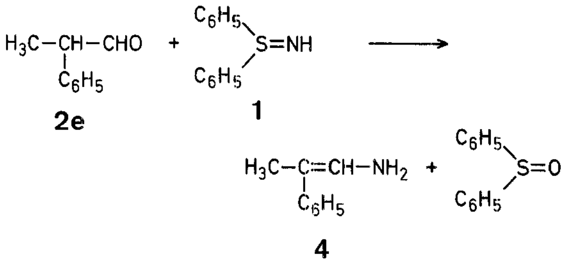
We found that *N*-unsubstituted *S*,*S*-diphenylsulfilimine can react with the carbonyl carbon of aldehydes and we describe here the results obtained.

The reaction of *N*-unsubstituted diphenylsulfilimine (**1**) with benzaldehyde, cinnamaldehyde (*E* configuration), and pyridine-3-carboxaldehyde in benzene and with 2,2-dimethylpropanal in benzene or dimethyl sulfoxide gave the nitriles (**3**) corresponding to the aldehydes **2** in good to excellent yields. This reaction presumably involves the carbonyl addition of the sulfilimine **1** to the carbonyl group of **2**, followed by elimination of diphenyl sulfoxide via a four-centered transition state, and oxidation of the intermediate imine:



The mild reaction conditions, the simplicity of performance, and the good yields make this reaction a useful method for the conversion of aldehydes to nitriles.

2-Phenylpropanal (**2e**) reacts with diphenylsulfilimine (**1**) in benzene to give the enamine **4** the structure of which was established by spectral data and by comparison with an authentic sample.



This reaction confirms the suggested mechanism; in this case, isomerization of the intermediate imine to the corresponding enamine (**4**) proceeds faster than its oxidation to the nitrile.

The reactions of sulfilimine **1** with crotonaldehyde (**2f**, *E*-configuration) and 3-methyl-2-butenal (**2g**) in benzene afford the 2-cyanoaziridines **5f** and **5g**, respectively.

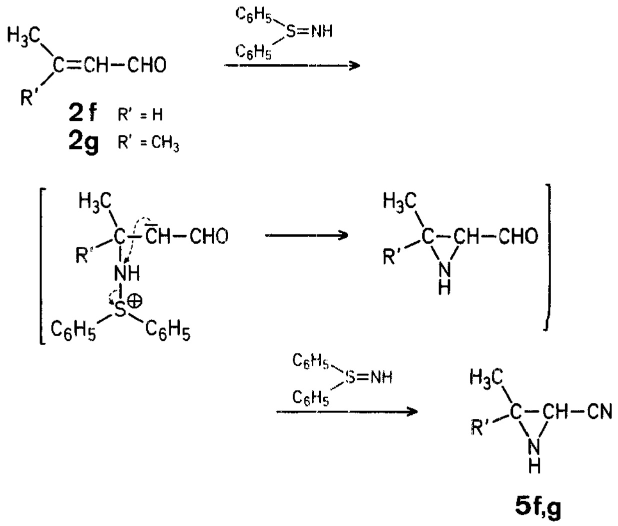
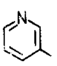
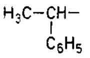
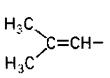


Table. Reaction of Diphenylsulfilimine (**1**) with Aldehydes (**2**)

R in **2**	Product	Yield[a] [%]	b.p./torr or m.p. [°C] found	reported[9]	I.R. (film) [cm⁻¹]	¹H-N.M.R. (CDCl₃) δ [ppm]
C_6H_5	**3a**	84[b]	b.p. 72–75°/8	b.p. 190.7°/760	2250, 1600	
$C_6H_5-CH=CH-$	**3b**	80[b]	b.p. 128–130°/8	b.p. 134–136°/12	2200, 1620, 1590	7.10–7.50 (m, 6H); 5.70 (d, *J* = 17 Hz, 1H)[c]
	**3c**	87	m.p. 49–51°	m.p. 50–51°	2240, 1580	
t-C_4H_9	**3d**	66[b]	b.p. 94–98°/730	b.p. 105–106°/760	2240[d]	
 $H_3C-CH(C_6H_5)-$	**4**	40	[e,f]		3250, 1610, 1590	7.20–8.10 (m, 7H); 2.60 (s, 3H)
$H_3C-CH=CH-$	**5f**	43[b,g]	[e]		3320, 2260[h]	1.30 (d, *J* = 5.8 Hz, 3H); 2.13 (d, *J* = 3 Hz, 1H); 2.45 (s, 1H); 2.62 (dq, *J* = 5.8 and 3 Hz, 1H)[h]
 $(H_3C)_2C=CH-$	**5g**	85	[i]	$C_5H_8N_2$[j] (96.1)	3310, 3280, 2270	2.30 (s, 1H); 1.53 (broad s, 1H); 1.42 (s, 3H); 1.28 (s, 3H)

[a] Yield of pure isolated products, after distillation or chromatography on silica gel.
[b] Purity of products >98% as determined by G.L.C. analysis (10% DEGS on chromosorb W).
[c] *E* Configuration.
[d] In CCl_4 solution.
[e] Oil; compound purified by chromatography on silica gel and identified by I.R. and ¹H-N.M.R. spectral comparison with authentic material.
[f] Authentic material prepared according to Ref.[10].
[g] 11/1 Mixture of *trans* and *cis* isomers; authentic material prepared according to Ref.[7].
[h] Pure *trans* isomer.
[i] Oil.
[j] C 62.50 H 8.33 N 29.17
62.66 8.26 29.22
¹³C-N.M.R. ($CDCl_3$): δ = 22.091, 24.624, 27.938, 39.244, 118.575 ppm.

The structure of **5f** was established on the basis of spectral data and by comparison with an authentic sample prepared according to Ref.[7]. The crude product **5f** was an 11/1 mixture of the *trans* and *cis* isomers as determined by G.L.C. and ^{1}H-N.M.R. data. Aziridine **5g** was identified by spectral data (I.R., ^{1}H- and ^{13}C-N.M.R.) and element analysis.

Since we found that no reaction takes place between 2-butenenitrile (crotononitrile) or 3-methyl-2-butenenitrile and sulfilimine **1** these nitriles cannot be precursors of aziridines **5f, g**. A Michael-type addition of sulfilimine **1** to the C=C double bond of aldehydes **2f, g** followed by an intramolecular displacement reaction (see above scheme) should hence account for aziridine formation; sulfilimine **1** then reacts with the carbonyl group to give nitriles **5f, g**.

Diphenylsulfilimine is prepared following a known procedure[8].

Benzonitrile from Benzaldehyde; Typical Procedure:

A solution of diphenylsulfilimine (**1**; 4.4 g, 22 mmol) and benzaldehyde (1.2 g, 11 mmol) in benzene (100 ml) is refluxed for 24 h. The solvent is then removed under reduced pressure and the residual crude product distilled in vacuo to afford pure benzonitrile; yield: 0.95 g (84%); b.p. 72–75 °C/8 torr (Ref.[9], b.p. 190.7 °C/760 torr).

2,2-Dimethylpropanenitrile (3d):

A solution of diphenylsulfilimine (**1**; 4 g, 20 mmol) and 2,2-dimethylpropanal (**2d**; 0.86 g, 10 mmol) in dimethyl sulfoxide (40 ml) is stirred overnight at 80–85 °C. To the cold solution, ice/water (30 ml) is added and the mixture is extracted with ether (5 × 40 ml). The extract is washed with water (2 × 50 ml) and dried with magnesium sulfate. The solvent is evaporated and the residual crude product distilled; yield: 0.55 g (66%); b.p. 94–98 °C/730 torr (Ref.[9], b.p. 105–106 °C/760 torr).

Received: January 7, 1980
(Revised form: May 2, 1980)

---

* Address for correspondence.

[1] Y. Tamura et al., *J. Org. Chem.* **38**, 4324 (1973).

[2] Y. Tamura, H. Matsushima, M. Ikeda, *Tetrahedron* **32**, 431 (1976).

[3] N. Furukawa, S. Oae, *Synthesis* **1976**, 30.

[4] T. L. Gilchrist, C. J. Moody, *Chem. Rev.* **77**, 409 (1977).

[5] N. Furukawa et al., *Tetrahedron* **36**, 73 (1980).

[6] J. A. Franz, J. C. Martin, *J. Am. Chem. Soc.* **97**, 583 (1975).

[7] K. Burzin, K. Enderer, *Angew. Chem.* **84**, 108 (1972); *Angew. Chem. Int. Ed. Engl.* **11**, 151 (1972).

[8] N. Furukawa et al., *Tetrahedron Lett.* **1972**, 1619.
T. Yoshimura, T. Omata, N. Furukawa, S. Oae, *J. Org. Chem.* **41**, 1728 (1976).

[9] *Handbook of Chemistry and Physics*, 45th Ed., R. C. West, ed., Chemical Rubber Co., Cleveland, Ohio, 1964–1965.

[10] W. Krabbe, A. Seher, E. Polzin, *Ber. Dtsch. Chem. Ges.* **74**, 1892 (1941).
A. Seher, *Arch. Pharm. (Weinheim)* **284**, 371 (1951).

0039-7881/80/1232-1007 $ 03.00