

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

INTRAMOLECULAR TRAPPING OF THE NITRENE GENERATED BY PHOTOLYSIS OF *S, S*-DIPHENYL *N*-ACYLSULFILIMINE

Naomichi Furukawa^a; Mitsuo Fukumura^a; Takehiko Nishio^a; Shigeru Oae^a

^a Department of Chemistry, University of Tsukuba, Niihari-gun, Ibaraki

To cite this Article Furukawa, Naomichi , Fukumura, Mitsuo , Nishio, Takehiko and Oae, Shigeru(1978) 'INTRAMOLECULAR TRAPPING OF THE NITRENE GENERATED BY PHOTOLYSIS OF *S, S*-DIPHENYL *N*-ACYLSULFILIMINE', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 5: 2, 231 — 237

To link to this Article: DOI: 10.1080/03086647808069891

URL: <http://dx.doi.org/10.1080/03086647808069891>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

INTRAMOLECULAR TRAPPING OF THE NITRENE GENERATED BY PHOTOLYSIS OF *S,S*-DIPHENYL *N*-ACYLSULFILIMINE

NAOMICHI FURUKAWA, MITSUO FUKUMURA, TAKEHIKO NISHIO
and SHIGERU OAE

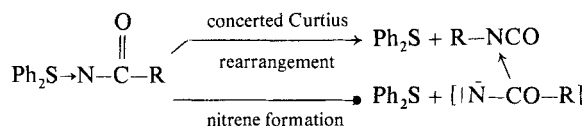
Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 300-31

(Received May 15, 1978)

Various *N*-acyldiphenylsulfilimines (Ia-k) were found to undergo photolysis in argon atmosphere, to afford the corresponding isocyanates, diphenyl sulfide and diphenyl disulfide. Attempts to trap intramolecularly the acylnitrene with olefinic linkage or sulfide afforded small amounts of the trapped products, whereas photolysis of *N*-mesityldiphenylsulfilimine (Ia) afforded a C-H inserted product of the nitrene in a substantial yield together with the isocyanate. Benzophenone-sensitized photolysis of Ia indicates that the nitrene generated is a singlet species.

Sulfilimine is isoelectronic to sulfoxide and has a semipolar S—N bond¹ which can be cleaved readily in such reactions as nucleophilic substitutions on the trivalent sulfur atom,^{2,3} the Pummerer-type reaction,³ treatment with elemental sulfur⁴ or thiols.⁵ However, *N*-acyldiphenylsulfilimines are quite stable and pyrolysis of *N*-tosyldiphenylsulfilimine takes place only upon heating at above 200°C for a long time,⁶ although even thermally stable *N*-acylsulfilimines were found to be photolyzed readily to afford complex mixtures of product.⁷

Recently, we also found that *N*-acyldiphenylsulfilimines undergo photolysis and afford the corresponding isocyanates in high yields.⁸ A question remains whether the isocyanate is produced via the concerted Curtius-type rearrangement or by initial S—N bond fission to generate the nitrene which in the subsequent steps undergoes 1,2-shift of the R group to the terminal nitrogen to afford the isocyanates, as shown below.



Recently, Swern and coworkers⁷ reported the generation of the corresponding nitrenes in the photolysis of *S,S*-dimethyl-*N*-benzoyl and *N*-ethoxycarbonylsulfilimines by trapping them with cyclohexene. We also confirmed the formation of the nitrene in the photolysis of *N*-acyldiphenylsulfi-

mine by trapping with cyclohexene to afford the corresponding aziridine. Gilchrist and Rees⁹ also proposed the formation of nitrene in both photolysis and thermolysis of various *N*-substituted sulfilimines. In order to obtain further information on the nature of nitrene thus generated by the photolysis of various sulfilimines and to inquire into the possible use of the photolysis of sulfilimine for organic syntheses, we prepared several *N*-acyldiphenylsulfilimines having functional groups which can trap intramolecularly the nitrenes generated *in situ*. When the sulfilimine having a terminal olefinic linkage or mesityl group was photolyzed, either the intramolecular addition or C—H insertion product was actually obtained. This paper describes preparations of several *N*-acylsulfilimines of a new type and their photolyses.

RESULTS AND DISCUSSION

The following *N*-acyldiphenylsulfilimines were prepared according to our method by using *N*-unsubstituted diphenylsulfilimine and appropriate acylating agents.¹⁰ The sulfilimines thus obtained are shown in Table I together with the spectral data and elemental analyses.

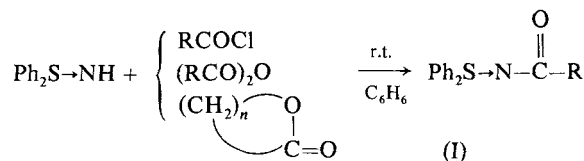


TABLE I
Physical properties of *N*-acyldiphenylsulfilimines

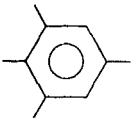
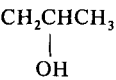
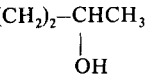
R in (I)	Yield (%)	m.p. (°C)	ir (cm ⁻¹)	nmr (δ , ppm, CDCl ₃)	Elemental analysis (%)		
a 	52.0	143–144	3050, 1610, 1580 1560, 1480, 1445 1320, 1175, 1100 860	7.92–7.67 (m, 4H) 7.57–7.33 (m, 6H) 6.77 (s, 2H) 2.33 (s, 6H) 2.22 (s, 3H)	C ₂₂ H ₂₁ SNO C Calcd. 76.00 Found 76.00	H N 6.09 5.93	4.03 4.03 3.99
b CH ₂ Ph	59.8	120–121	3050, 1590, 1570 1445, 1315, 1135	7.80–7.19 (m, 15H) 3.77 (s, 2H)	C ₂₀ H ₁₇ SNO C Calcd. 75.21 Found 75.27	H N 5.37 5.36	4.39 4.12
c (CH ₂) ₂ -Ph	48.3	71–72	3050, 1585, 1570 1470, 1440, 1340 1310	7.70–7.17 (m, 15H) 3.23–2.63 (m, 4H)	C ₂₁ H ₁₉ SNO C Calcd. 75.64 Found 75.79	H N 5.74 5.47	4.20 4.35
d CH=CH ₂	47.2	87–88	3050, 1630, 1580 1560, 805	7.90–7.30 (m, 10H) 6.53–6.33 (m, 2H) 5.67–5.43 (m, 1H)	C ₁₅ H ₁₃ SNO C Calcd. 70.56 Found 70.54	H N 5.13 5.20	5.49 5.41
e CH ₂ -CH=CH ₂	37.2	liquid	3050, 1635, 1590 1570, 810	7.90–7.30 (m, 10H) 6.37–5.77 (m, 1H) 5.33–4.93 (t, 2H) 3.27 (q, 2H)	C ₁₆ H ₁₅ SNO C Calcd. 71.34 Found 71.32	H N 5.61 5.61	5.20 5.23
f (CH ₂) ₂ -CH=CH ₂	53.3	55–56	3050, 1630, 1580 1560	7.90–7.27 (m, 10H) 6.13–5.69 (m, 1H) 5.33–4.80 (m, 2H) 2.67–2.33 (m, 4H)	C ₁₇ H ₁₇ SNO C Calcd. 72.05 Found 72.04	H N 6.05 6.13	4.94 4.89
g (CH ₂) ₃ -CH=CH ₂	40.6	88–89	3050, 1635, 1585 1570, 805	7.93–7.20 (m, 10H) 5.80–5.43 (m, 1H) 5.13–4.73 (m, 2H) 2.53–1.63 (m, 6H)	C ₁₈ H ₁₉ SNO C Calcd. 72.84 Found 72.69	H N 6.46 6.44	4.57 4.71
h 	63.8	liquid	3040, 1590, 1560 850	7.97–7.23 (m, 10H) 4.87 (brd, 1H) 4.40–3.93 (m, 1H) 2.63 (d, 2H) 1.23 (d, 3H)	C ₁₇ H ₁₉ SNO C Calcd. 67.75 Found 67.74	H N 6.35 6.36	4.65 4.60
i 	51.0	97–99	3050, 3420, 1580 1560, 805	8.0–7.3 (m, 10H) 4.2–3.6 (m, 2H) 2.72 (t, 2H) 1.90 (t, 2H) 1.20 (d, 3H)	C ₁₇ H ₁₉ SNO C Calcd. 67.75 Found 67.74	H N 6.35 6.36	4.65 4.60

TABLE I—contd.

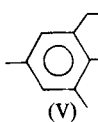
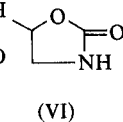
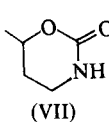
	R in (I)	Yield (%)	m.p. (°C)	ir (cm ⁻¹)	nmr (δ, ppm, CDCl ₃)	Elemental analysis (%)		
j	CH ₂ SCH ₃	55	liquid	3050, 1590, 1570 1475, 1440, 1310	7.80–7.23 (m, 10H) 3.38 (s, 2H) 2.23 (s, 3H)	C ₁₅ H ₁₅ S ₂ NO C	H	N
						Calcd. 62.25	5.22	4.83
						Found 62.00	5.11	5.08
k	(CH ₂) ₂ —SCH ₃	56	liquid	3050, 1590, 1570	7.83–7.23 (m, 10H) 2.90–2.73 (m, 4H) 2.13 (s, 3H)	C ₁₆ H ₁₇ S ₂ NO C	H	N
						Calcd. 63.33	5.64	4.61
						Found 63.51	5.70	4.84

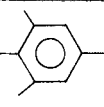
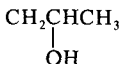
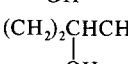
These sulfilimines (Ia–k) were irradiated with a low pressure mercury lamp through a quartz filter in benzene or methylene chloride solution under argon atmosphere for 3–8 h. The products obtained were

separated by column- or gas-chromatography and identified by either comparing the glc retention time or such spectral analyses as ir, nmr and mass spectroscopies. The results are summarized in Table II.

TABLE II

Yields of the photo-products of N-acyldiphenylsulfilimines (Ia–k) (%)

$\text{Ph}_2\text{S} \rightarrow \text{NCOR} \xrightarrow{h\nu} \text{R-NCO} + \text{Ph}_2 + \text{Ph}_2\text{S} + \text{Ph}_2\text{S}_2 + \text{PhNHCONHR}$									
(I)	(II)	(III)	(V)	(VI)	(VII)				

R	(I)	Solv.	h	(II)	Phz	PhzS	PhzSz	(III)	(V)	(VI)	(VII)
a	 (sens)	C ₆ H ₆ CH ₂ Cl ₂ CH ₂ Cl ₂	3 3 3	34.4 26.6 25.6	13.8 trace trace	39.0 46.2 40.0	trace 13.8 10.7		36.8 25.4 trace		
b	CH ₂ Ph	C ₆ H ₆ THF	3 3	52.4 41.3	14.3 trace	30.2 28.6	trace 12.2	27.4			
c	(CH ₂) ₂ Ph	C ₆ H ₆	3	60.8	13.7	39.2	trace	15.9			
d	CH=CH ₂	C ₆ H ₆	8	c	2.1	24.2	trace				
e	CH ₂ CH=CH ₂	C ₆ H ₆	8	c	17.1	26.1	5.4				
f	(CH ₂) ₂ CH=CH ₂	C ₆ H ₆	8	c	10.4	34.0	5.7	29.2			
g	(CH ₂) ₃ CH=CH ₂	C ₆ H ₆	8	c	17.9	34.0	trace	26.0			
h		C ₆ H ₆	7	0	13.4	41.4	4.1			59.8 ^b	
i		C ₆ H ₆	7	0	6.6	48.9	trace				41.9 ^b
j	CH ₂ -S-CH ₃	C ₆ H ₆	4	c	3.1	37.8	trace	8.0			
k	(CH ₂) ₂ -S-CH ₃	C ₆ H ₆	4	c	5.1	43.6	trace	9.0			

^a The yield was determined by glc.

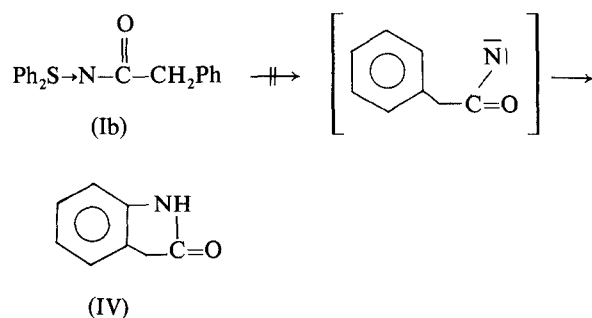
^b The yield was determined by nmr.

^c Isocyanate was identified by ir.

Inspection of the results reveals the following characteristic features of the photolysis.

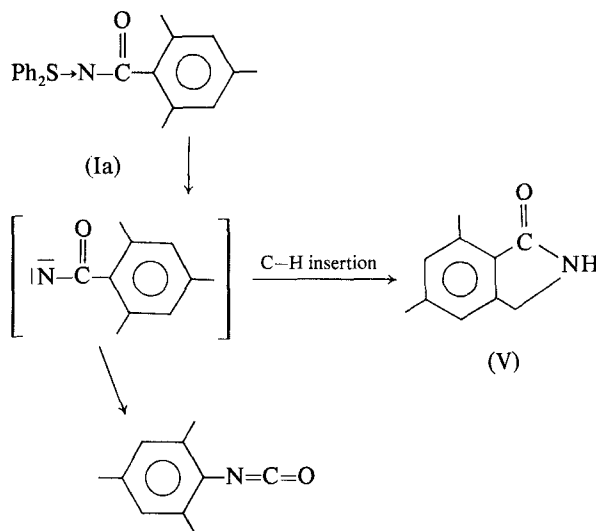
1) With all the systems the corresponding isocyanates, biphenyl, diphenyl sulfide and diphenyl disulfide were obtained in substantial yields except in the cases of (Ih) and (Ii). Furthermore, the isocyanates (IIb-c, IIf-g, IIj-k) were trapped with aniline to afford the corresponding urea derivatives (IIIb-c, IIIf-g, IIIj-k).

2) Photolysis of the *N*-phenylacetyl derivative afforded the normal photo-Curtius products, i.e., benzyl isocyanate and diphenyl sulfide in 52.4 and 30.2% yields, respectively, but failed to give such a -C-H insertion product as a lactam derivative (IV), although the corresponding nitrene would possibly insert into the -C-H bond as shown below.¹¹



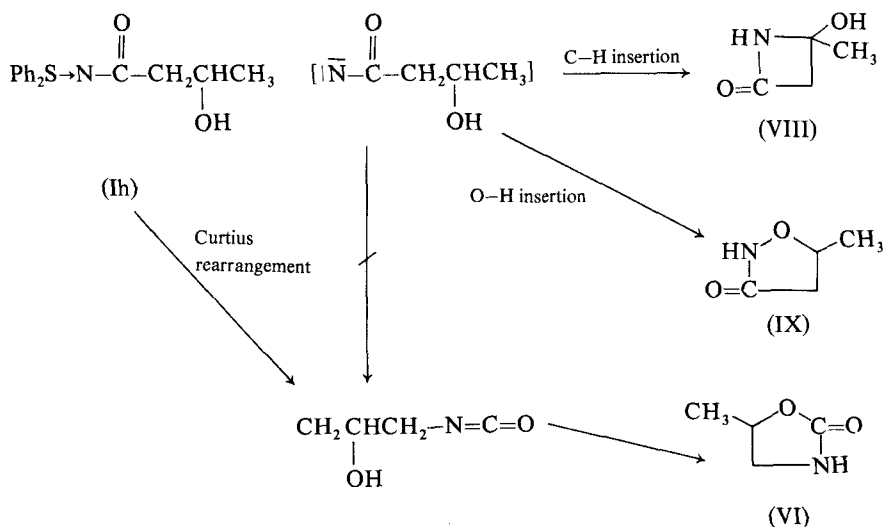
3) However, upon photolysis of the *N*-mesitylsulfilimine (Ia) a benzopyrrolidone (V), the nitrene-inserted product into *o*-CH₃ group, was obtained in

36.8% yield together with the normal Curtius product, mesityl isocyanate, as shown below.



On the other hand, when photolysis of (Ia) was carried out in the presence of benzophenone, a triplet sensitizer, in methylene chloride, the yield of the Curtius product (isocyanate) did not change; however, the yield of (V) decreased to almost a trace, suggesting that this insertion product (V) is formed with the singlet nitrene⁷ but not with a triplet nitrene.

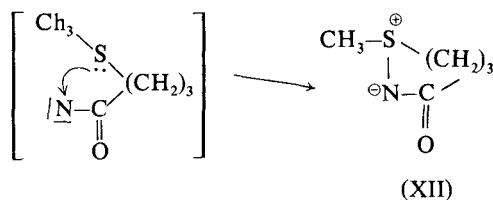
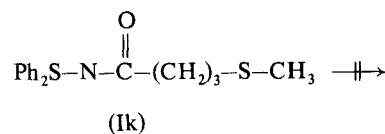
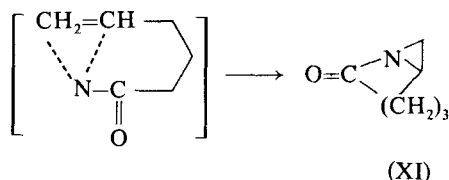
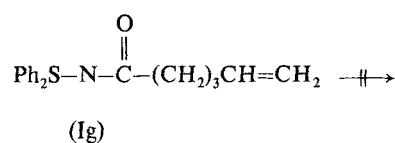
4) The photolyses of *N*-(3-hydroxy)butenyl- and *N*-(4-hydroxy)pentanoyldiphenylsulfilimine (Ih,i) afforded the 5- or 6-membered cyclic lactone deri-



vatives (VI) and (VII) in good yields, respectively, instead of forming the nitrene-insertion products such as (VIII) and (IX). The structure of (VIII) can be excluded readily by the spectral analysis. The choice between the two structures (VI) or (IX) can be made by inspection of the nmr pattern after the compound is treated with D₂O in order to remove the complex coupling with amide proton. The ¹H-nmr pattern of 4-position of the product was simplified upon treatment of the product with D₂O. If the structure of the product is (IX), the nmr signals should not change by exchanging the amide proton with deuterium. Therefore, the cyclic product obtained has the structure (VI).

This result demonstrates clearly the facile formation of the isocyanate which then reacts intramolecularly with the O-H group to afford the compound (VI). The formation of (VII) from (Ii) can be explained by a similar process to the formation of (VI). Apparently, these intramolecular trapping experiments with the OH group of the isocyanates are consistent with the results in which the isocyanates could not be detected or trapped after the reaction even in the presence of aniline.

5) Photolysis of the sulfilimine having terminal olefins (Id-g) or sulfides (Ij,k) did not give any intramolecular addition compounds like (XI) or (XII).



Only in the case of (Ig), a trace amount of the compound having such a structure as (XI) was obtained and identified from the ir spectrum which shows an absorption band at 1700 cm⁻¹ corresponding to the lactam structure. Instead of affording the addition products of the nitrene, (If) and (Ig) gave photo-Curtius products.

EXPERIMENTAL

Preparation of sulfilimine (Ia-k) was carried out by known methods starting from free diphenyl sulfilimine and various acylating agents.¹⁰ The yields, m.p. and spectral data are summarized in Table I.

N-(4-hydroxyvaleroyl)-S,S-diphenyl sulfilimine (Ii)¹⁰ was prepared according to the method previously reported, m.p. 97–99°C.

N-3-methylthioacetyl-S,S-diphenyl sulfilimine (Ij). 3-Methyl-mercaptopropionic acid¹² was prepared from chloroacetic acid and sodium methylthiolate in MeOH–H₂O solvent at room temperature. This acid was chlorinated with thionyl chloride and the chlorinated compound was treated with diphenyl sulfilimine as above. Ij was purified by column chromatography over silica gel eluted with chloroform in 55.0% yield.

Photolysis of N-mesityl-S,S-diphenyl sulfilimine. A solution of the sulfilimine (Ia, 300 mg) in dry benzene (30 ml) or methylene chloride (30 ml) containing 152 mg benzophenone was irradiated in a quartz vessel in argon for 3 h at room temperature. The products, biphenyl, diphenyl sulfide and diphenyl disulfide were identified by comparison of their glc retention times with those of the authentic samples. When the corresponding isocyanates could not be detected due to the overlapping of the glc retention time of these isocyanates with that of the solvent, as in the cases of sulfilimines having a terminal double bond (Id-g, j-k), aniline was added to the reaction mixture after the photolysis and the corresponding urea derivatives (IIIf-g, j-k) were obtained in 29.2 and 26.0% yields, respectively, indicating the initial formation of the corresponding isocyanates. Furthermore, mesityl isocyanate was isolated by glc (TCD column SE-30 2 m × 2 mm, column temp. 130°C, He 1.6 kg/cm²). 4,6-Dimethyl-1-indolinone was obtained by column chromatography over silica-gel eluted with chloroform-methanol (14:1).

Mesityl isocyanate (IIa)¹³

mp (°C) 45–46
ir (cm⁻¹) 3050, 2270,
nmr (δ, ppm, CDCl₃) 6.77 (s, 2H) 2.23 (s, 9H)

4,6-Dimethyl-1-indolinone (V)

mp (°C) 166–167 (lit¹⁴ 166.5–168°C)
ir (cm⁻¹) 3180, 3060, 1690,
nmr (δ, ppm, CDCl₃) 7.83–7.40 (br, NH) 6.97 (s, 2H) 4.30 (s, 2H) 2.64 (s, 3H) 2.36 (s, 3H)

C ₁₀ H ₁₁ NO	C	H	N
Calcd.	74.51	6.88	8.69
Found	74.34	6.81	8.41

Benzyl isocyanate (IIb) was isolated by glc (TCD column SF-96 2 m × 2 mm, column temp 130°C, He 1.0 kg/cm²)
bp 118°C/200 mmHg¹⁴
ir (cm⁻¹) 3050, 2270,
nmr (δ, ppm, CDCl₃) 7.37 (s, 5H) 4.50 (s, 2H)

N-Phenyl-N-benzyl urea (IIIb) was purified by column chromatography over silica-gel eluted with benzene: ethyl acetate = 19:1.
mp (°C) 165–166
ir (cm⁻¹) 3300, 1640
nmr (δ, ppm, CDCl₃) 7.40–6.83 (m, 11H) 5.60 (br, NH) 4.30 (d, 2H)
(NH protons did not appear clearly because of its small solubility in CDCl₃)

C ₁₄ H ₁₄ N ₂ O	C	H	N
Calcd.	74.31	6.24	12.38
Found	74.11	6.52	12.51

β-Phenylpropyl isocyanate (IIc) was isolated by glc (TCD column SE-30 1 m × 2 mm, column temp 80°C, He 0.7 kg/cm²)
bp 104–106°C/15 mmHg¹⁵
ir (cm⁻¹) 3050, 2275,
nmr (δ, ppm, CDCl₃) 7.23 (s, 5H) 3.57 (t, 2H) 2.90 (t, 2H)

N-(β-phenyl)ethyl-N-phenyl urea (IIIc) was purified by column chromatography over silica-gel eluted with benzene: ethyl acetate = 19:1.
mp (°C) 152.5–153.5
ir (cm⁻¹) 3300, 1650, 1600, 1570
nmr (δ, ppm, CDCl₃) 7.37–6.93 (m, 11H) 6.60 (br, NH) 3.43 (t, 2H) 2.77 (t, 2H)
(NH protons did not appear clearly because of its small solubility in CDCl₃)

C ₁₅ H ₁₆ N ₂ O	C	H	N
Calcd.	74.97	6.71	11.65
Found	75.00	6.82	11.56

N-4-Butenyl-N-phenyl urea (IIIf) was purified by column chromatography through silica-gel eluted with benzene: ethyl acetate = 4:1.
mp (°C) 86–87
ir (cm⁻¹) 3340, 3030, 1640
nmr (δ, ppm, CDCl₃) 7.53 (br, NH) 7.43–6.67 (m, 5H) 6.03–5.30 (m, 2H) 5.30–4.73 (m, 2H) 3.47–3.03 (m, 2H) 2.40–1.90 (m, 2H)

C ₁₁ H ₁₄ N ₂ O	C	H	N
Calcd.	69.45	7.42	14.73
Found	69.40	7.25	14.68

N-5-Hexenyl-N-phenyl urea (IIIg) was purified by column chromatography through silica-gel eluted with benzene: ethyl acetate = 4:1
mp (°C) 62–63
ir (cm⁻¹) 3300, 1640, 920
nmr (δ, ppm, CDCl₃) 7.60 (br, NH) 7.37–6.90 (m, 5H) 5.80–5.50 (m, 1H) 5.13–4.80 (m, 2H) 3.27–2.97 (m, 2H) 2.17–1.33 (m, 4H)

C ₁₂ H ₁₅ N ₂ O	C	H	N
Calcd.	70.55	7.89	13.71
Found	70.53	7.73	13.66

5-Methyl-2-oxazolidone (VI) was purified by column chromatography through silica-gel eluted with chloroform.
bp 111–113°C/1 mmHg¹⁶
ir (cm⁻¹) 3290, 1740
nmr (δ, ppm, CDCl₃) 6.55 (br, NH) 5.00–4.43 (m, 1H) 3.83–2.97 (m, 2H) 1.40 (d, 3H)

6-Methyl-1,3-oxazin-2-one (VII) was purified by column chromatography through silica-gel eluted with chloroform: methanol = 14:1.
mp (°C) 90–91
ir (cm⁻¹) 3250, 3100, 1700
nmr (δ, ppm, CDCl₃) 6.83 (br, 1 H) 4.67–4.20 (m, 1H) 3.43–3.23 (m, 2H) 2.17–1.72 (m, 2H) 1.40 (d, 3H)

C ₅ H ₉ NO ₂	C	H	N
Calcd.	52.16	7.88	12.17
Found	52.18	7.83	11.87

N-3-Methylthioacetyl-N-phenyl urea (IIIj) was purified by column chromatography through silica-gel eluted with ethyl acetate.
mp (°C) 126–127
ir (cm⁻¹) 3320, 1635, 1590, 1560
nmr (δ, ppm, CDCl₃) 7.23 (s, 5H) 6.07–5.83 (br, NH) 4.33 (d, 2H) 2.13 (s, 3H)

C ₉ H ₁₂ N ₂ OS	C	H	N
Calcd.	55.07	6.16	14.27
Found	55.20	6.15	13.99

N-2-Methylthioethyl-N-phenyl urea (IIIk) was purified by column chromatography through silica-gel eluted with ethyl acetate.
mp (°C) 97–98
ir (cm⁻¹) 3320, 1640, 1590
nmr (δ, ppm, CDCl₃) 7.40–7.20 (m, 5H) 6.01–5.60 (br, NH) 3.40 (t, 2H) 2.60 (t, 2H) 2.06 (s, 3H)

C ₁₆ H ₁₄ N ₂ OS	C	H	N
Calcd.	57.11	6.71	13.32
Found	57.33	6.60	13.16

REFERENCES

1. See S. Oae, *Organic Chemistry of Sulfur* (Plenum Press, 1977) Chapter 8; A. Kalman, B. Duffin and A. Kucsman, *Acta. Crystallogr. Sect. B*, **27**, 586 (1971); A. Kalman and K. Sasvari, *Cryst. Struct. Commun.*, **243** (1972); A. Kucsman, A. Kalman and I. Kapovits, *Acta. Chim. Acad. Sci. Hung.* **53**, 97 (1967); A. Kalman, K. Sasvari and A. Kucsman, *Chem. Commun.* 1447 (1971); A. Kalman, K. Sasvari and A. Kucsman, *Acta Crystallogr. Sect. B*, **29**, 1241 (1973).
2. D. C. Garwood, M. R. Johnes and D. J. Cram, *J. Am. Chem. Soc.* **95**, 1925 (1973); F. G. Yamagishi, D. R. Rayner, E. T. Zwicker and D. J. Cram, *J. Am. Chem. Soc.* **95**, 1916 (1973); S. Oae, T. Aida and N. Furukawa, *Int. J. Sulfur Chem.* **8**, 401 (1973).
3. T. L. Gilchrist and C. J. Moody, *Chem. Rev.* **77**(3), 409 (1977).
4. S. Oae, Y. Tsuchida and N. Furukawa, *Bull. Chem. Soc., Japan*, **45**, 2856 (1972).

5. S. Oae, T. Aida, M. Nakajima and N. Furukawa, *Tetrahedron*, **30**, 947 (1974); T. Aida, N. Furukawa and S. Oae, *Tetrahedron Lett.* 4255 (1971).
6. T. Aida, N. Furukawa and S. Oae, *J. Chem. Soc. Perkin II* 1433 (1976).
7. Y. Hayashi and D. Swern, *Tetrahedron Lett.* 1921 (1972); Y. Hayashi and D. Swern, *J. Am. Chem. Soc.* **95**, 5205 (1973).
8. N. Furukawa, T. Nishio and S. Oae, *J. Chem. Soc. Perkin I*, 96, (1977).
9. T. L. Gilchrist, C. J. Moody and C. W. Rees, *J. Chem. Soc. Perkin I*, 1964 (1975); See reviews, T. L. Gilchrist and C. J. Moody, *Chem. Revs.* **77**, 409 (1977).
10. T. Yoshimura, T. Omata, N. Furukawa and S. Oae, *J. Org. Chem.* **41**, 1728 (1976); Y. Tamura, K. Sumoto, H. Matsushima, H. Taniguchi and M. Ikeda, *J. Org. Chem.* **38**, 4324 (1973).
11. I. Brown and O. E. Edwards, *Can. J. Chem.* **47**, 2751 (1969).
12. A. Mooradian, C. J. Cavallit, A. J. Bergman, E. J. Lawson and C. M. Suter, *J. Am. Chem. Soc.* **71**, 3372 (1949).
13. G. Just and W. Zehetner, *Tetrahedron Lett.* 3389 (1967).
14. A. J. Hill and W. M. Degnan, *J. Am. Chem. Soc.* **62**, 1595 (1940).
15. H. Pelster and D. Delts, *Belg.* **631**, 961 (1963); *Chem. Abstr.* **61**(2), 6919 h (1964).
16. M. E. Dyen and D. Swern, *Chem. Revs.* **67**, 197 (1967).