

Photochemical Isomerization of *O*-Allyl and *O*-But-3-enyl Thiocarbamates

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The photochemistry of *O*-allyl and *O*-but-3-enyl thiocarbamates has been studied. Photolysis of benzene solutions of *O*-allyl *N*-phenylthiocarbamates gave *S*-allyl *N*-phenylthiocarbamates. The 1,3-allyl migration from the oxygen to the sulfur involves a concerted process. The same type of 1,3-migration took place in the conversion of *O*-benzyl *N*-phenylthiocarbamate into *S*-benzyl *N*-phenylthiocarbamate. Irradiation of *O*-but-3-enylthiocarbamates produced iminoxolanes *via* aminothietane intermediates. In the case of *O*-but-3-enyl *N*-benzoyl-*N*-phenylthiocarbamates, 3-(benzoylsulfanylmethyl)-2-phenyliminoxolanes were obtained *via* a ring opening of the aminothietanes involving a 1,5-benzoyl shift.

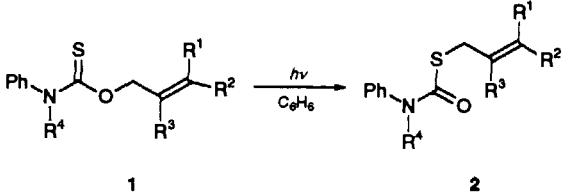
Photochemical studies of thiocarbonyl compounds have received much attention from both mechanistic and the synthetic points of view since their photochemical behaviour differs from that of the corresponding carbonyl derivatives.¹ In particular, 2 + 2 photocycloaddition of thioamides² and thioimides³ to alkenes have been well studied; they give thietanes as primary products which are often unstable and transform to rearrangement and fragmentation products. Compounds with a thiocarbonyl adjacent to two heteroatoms have different electronic conditions from thioketones and thioesters; their photochemical behaviour has become of interest to us. Recently Nishio *et al.* reported photochemical reactions of benzocyclic dithiocarbamates and thiocarbamates, including benzothiazole-2-thiones and benzoxazole-2-thiones, with electron-deficient alkenes leading to intermolecular cycloaddition followed by isomerization.⁴ In relation to our study on the photochemical reactions of thiocarbonyl compounds,^{3a,e-h,5} we now present the results of the photochemical reaction of *O*-allyl and *O*-but-3-enyl thiocarbamates, which yield *S*-allyl thiocarbamates and iminoxolane derivatives, respectively. The different photochemical behaviour is dependent on the length of the carbon chain between the thiocarbonyl and the alkenyl groups.

Results and Discussion

The *O*-alkenyl thiocarbamates were obtained from the reaction of the corresponding isothiocyanate and alcohol in the presence of triethylamine. When a benzene solution of *O*-allyl *N*-phenylthiocarbamate **1a** was irradiated under argon with a high pressure mercury lamp, *S*-allyl *N*-phenylthiocarbamate **2a**, the allyl migration product, was obtained in 72% yield; the structure was inferred from the spectral data. Furthermore, the structure was confirmed by direct comparison with an authentic sample synthesized from phenyl isocyanate and prop-2-ene-1-thiol. Photolysis of *O*-alk-2-enyl *N*-phenylthiocarbamates **1b** and **1c** and *O*-allyl *N*-benzoyl-*N*-phenylthiocarbamates **1d** and **1e** also gave the corresponding *S*-alk-2-enyl thiocarbamates **2b–e** (Table 1).

Plausible mechanisms leading to the allyl migration products are presented in Scheme 1. Path A involves the cleavage of the biradical or thietane formed by C–S bond formation. Path B involves radical pair formation by allyl–O bond cleavage. Path C includes a concerted [1,3] shift. The reaction mechanism can be determined from the result of the photolysis of *O*-but-2-enyl

Table 1 Photochemical reaction of *O*-alk-2-enyl *N*-phenylthiocarbamates **1a–c** and *O*-alk-2-enyl *N*-benzoyl-*N*-phenylthiocarbamates **1d** and **1e**



1					2	
	R ¹	R ²	R ³	R ⁴	Conv. (%)	Yields of 2 (%)
a	H	H	H	H	78	72
b	H	H	Me	H	100	39
c	H	Me	H	H	67	35
d	H	H	H	Bz ^a	100	40
e	H	H	Me	Bz ^a	92	60

^a Bz = benzoyl.

N-phenylthiocarbamate **1c**. If the allyl migration proceeds *via* a biradical or thietane, as in path A, then *S*-(1-methylprop-2-enyl) *N*-phenylthiocarbamate **3c** will be obtained as the photo-product. On the other hand, if the reaction proceeds *via* path B, then *S*-but-3-enyl and/or *S*-(1-methylprop-2-enyl) *N*-phenylthiocarbamate will be formed. In fact, irradiation of **1c** gave only the *S*-but-3-enyl derivative **2c**. Furthermore, the complete lack of allyl inversion would seem to be evidence against a radical pair mechanism (path B) and in favour of a concerted [1,3] shift (path C).

However, it is known that the pyrolysis of *S*-allyl dithiocarbamates leads to 3,3-sigmatropic rearrangement.⁶ When *O*-allyl thiocarbamates **1a–c** were heated to melting point, 3,3-sigmatropic rearrangement products **3a–c**† were obtained almost quantitatively.

1,3-Alkyl migration occurred in the photochemical reaction of *O*-benzyl *N*-phenylthiocarbamate **4a** to give *S*-benzyl *N*-phenylthiocarbamate in 85% yield at 80% conversion (Scheme 2). However, the *O*-methyl derivative **4b** was inert towards photolysis. Therefore, the 1,3-alkyl migration from the oxygen to the sulfur of thiocarbamates is facilitated by allyl and benzyl

† Thiocarbamates **3a** and **3b** are identical with **2a** and **2b**, respectively.

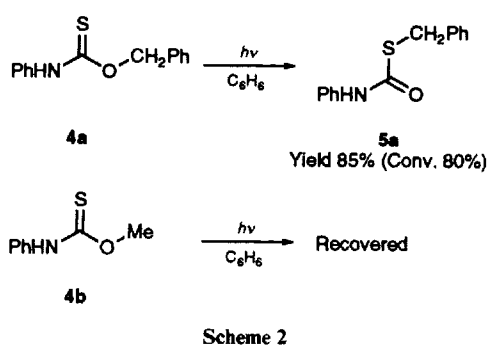
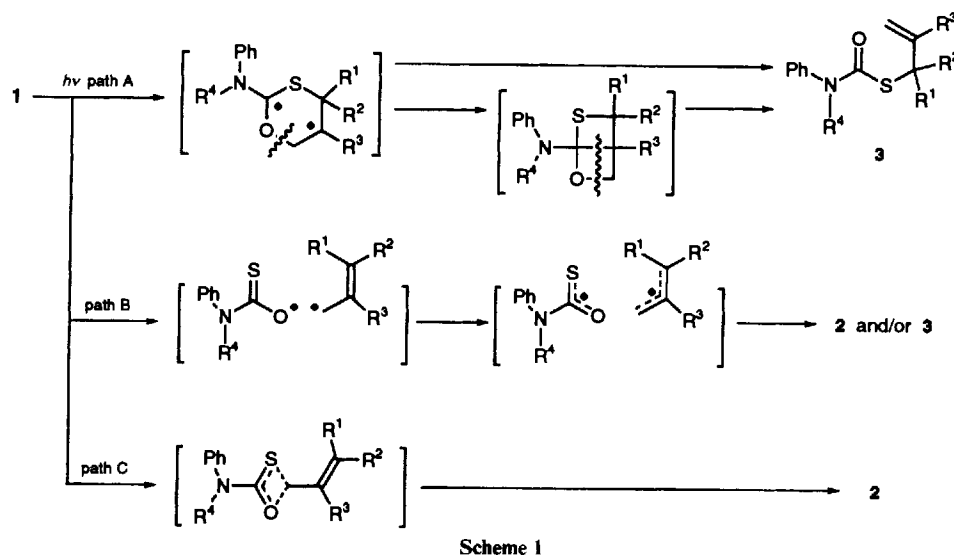
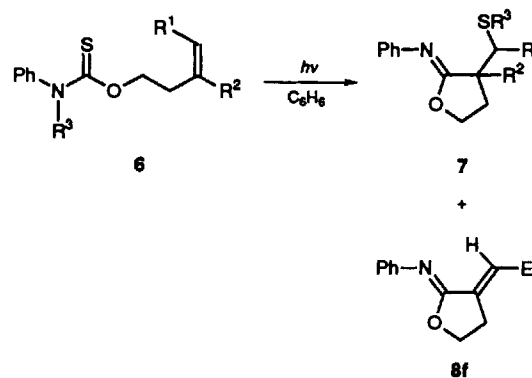


Table 2 Photochemical reaction of *O*-but-3-enyl *N*-phenylthiocarbamates **6**



6	R ¹	R ²	R ³	Conv. (%)	Yield (%) 7
a	H	H	H	83	50
b	H	Me	H	91	66
c	Et	H	H	55	39
d	H	H	Bz ^a	95	32
e	H	Me	Bz ^a	95	69
f	Et	H	Bz ^a	94	(22) ^b

^a Bz = benzoyl. ^b Yield of **8f**.

substituents, which are characterized by a lower bond dissociation energy.

The 1,3-allyl migration for **1a** was sensitized by Michler's ketone ($E_T = 62 \text{ kcal}^{-1}$; $1 \text{ cal} = 4.184 \text{ J}$).⁷ The migration was quite efficiently quenched by *trans*-stilbene ($E_T = 50 \text{ kcal}^{-1}$) and ferrocene ($E_T = 35 \text{ kcal}^{-1}$). These results indicate that this photoisomerization proceeds from the triplet excited state.

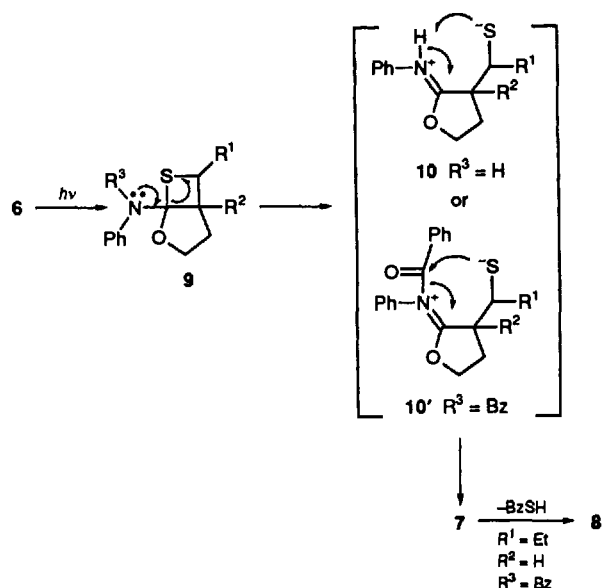
Next we attempted the photochemical reaction of thiocarbamates **5** possessing two carbons between the oxygen of the thiocarbamate chromophore and the alkenyl carbon. Photolysis of *O*-but-3-enyl *N*-phenylthiocarbamate **6a** under the same conditions gave 2-phenylimino-3-sulfanylmethyl-oxolane **7a** in 50% yield at 83% conversion (Table 2). The structure of **7a** was inferred from the spectral data. The IR spectrum exhibits a characteristic absorption at 1680 cm^{-1} attributable to the imino bond and the absence of an absorption derived from an N-H bond. The ¹H NMR spectrum shows a broad signal at $\delta 1.8$ assignable to the thiol proton and the absence of olefinic protons. The ¹³C NMR spectrum exhibits a singlet peak derived from C=N at $\delta 163.1$ and no signals which could be attributed to thiocarbonyl and olefinic carbons were observed. Furthermore, the presence of a triplet peak at $\delta 69.0$, assignable to C-5, excludes the possibility of the alternative pyrrolidinone structure. Photolysis of thiocarbamates **6b** and **6c** also gave the corresponding iminoxolanes **7b** and **7c**.

Irradiation of *N*-benzoyl derivatives **6d** and **6e** under the same conditions gave 3-(benzoylsulfanylmethyl)-2-phenyliminoxolanes **7d** and **7e** whereas the photolysis of *O*-[(*Z*)-hex-3-enyl] *N*-benzoyl-*N*-phenylthiocarbamate **6f** gave 3-propylidene-2-phenyliminoxolane **8f** in 22% yield. The structures of iminoxolanes **7d**, **7e** and **8f** were determined on the basis of spectral data. Furthermore, the structure of **7d** was confirmed

by the fact that iminoxolane **7d** was obtained quantitatively by the benzoylation of **7a** with benzoyl chloride in the presence of triethylamine. However, the molecular ion peak in the mass spectrum of **8f** shows that the molecule loses thiobenzoic acid from the starting material **6f**. The ¹³C NMR spectrum exhibits a new singlet at $\delta 128.7$ (C-3) and a doublet at $\delta 135.1$ (C-1') assignable to propylidene group.

The mechanism of formation of iminoxolanes **7** and **8** can be reasonably explained in terms of the intermediacy of a bicyclic aminothietane **9** (Scheme 3).[‡] The thietane easily opens to a zwitterion, facilitated by the lone pair of the nitrogen atom. Proton transfer of zwitterion **10** leads to imino-3-sulfanylmethyl-oxolane **7** and the 1,5-benzoyl shift of **10'** caused by the attack of the thiolate anion on the benzoyl carbonyl carbon

[‡] Aminothietanes are suggested as intermediates of the [2 + 2] cycloaddition of thioamides with alkenes, however, most of them are too unstable to isolate except for one example.²⁹



Scheme 3

S-benzoyl derivatives. Furthermore, it is concluded that the elimination of thiobenzoic acid from 7 leads to 3-propylidene-2-phenyliminoxolane 8.

A quenching experiment on the photochemical formation of 6 using *trans*-stilbene and ferrocene indicates that the photo-reaction proceeds from the triplet excited state as in the case of 1.

In conclusion, the intramolecular photochemical reaction of *O*-alkenyl thiocarbamates gave photoproducts in which the photoprocesses are defined by the length of the carbon chain between the oxygen and the alkenyl group attached to the thiocarbamate. Photolysis of *O*-allyl thiocarbamates which have one carbon between the oxygen and the alkenyl group promotes a concerted 1,3-allyl migration leading to *S*-allyl thiocarbamates. On the other hand, irradiation of *O*-but-3-enyl thiocarbamates in which the thiocarbonyl and the alkenyl group are separated by two carbons leads to [2 + 2] cycloaddition between the two functional groups giving bicyclic thietanes. 1-amino-2-oxa-7-thiabicyclo[3.2.0]heptanes, from which iminoxolanes were obtained *via* a zwitterionic intermediate. The photochemical reaction provides a useful synthesis of iminoxolanes and also reveals the mechanism for the 1,3-allyl migration from the oxygen to the sulfur of thiocarbamates.

Experimental

IR spectra of CHCl_3 solutions were recorded with a Shimadzu IR-420 spectrophotometer. ^1H and ^{13}C NMR spectra of CDCl_3 solutions were recorded with JEOL FX-270 and GSX-500 spectrometers, respectively. *J* Values are given in Hz. An Eikosya 1 kW high-pressure Hg lamp was used in the irradiations. Silica gel (Merck, Kieselgel 60, 230–400 mesh) was used for flash chromatography.

Preparation of *O*-Alkenyl *N*-Phenylthiocarbamates 1a–c, 4a, b and 6a–c.—All thiocarbamates were prepared by the reaction of phenyl isothiocyanate with the corresponding alkenyl alcohol. To the stirred alkenyl alcohol (24 mmol) was added phenyl isocyanate (20 mmol) and Et_3N (0.5 cm^3) and the reaction mixture was kept for 24 h at room temperature. The unchanged alcohol was evaporated off under reduced pressure and the residual mixture was subjected to chromatography on silica gel (eluent: benzene–hexane). The crystalline products were recrystallized from chloroform–hexane.

Preparation of *O*-Alkenyl *N*-Benzoyl-*N*-phenylthiocarbamates 1d, e and 6d–f.—To a stirred benzene solution of thiocarbamate (10 mmol) and triethylamine (12 mmol), was added benzoyl chloride (12 mmol) in benzene (10 cm^3) drop-by-drop, and the reaction mixture was stirred at room temperature overnight. The precipitated triethylamine hydrochloride was filtered off and the filtrate was concentrated under reduced pressure and the residual mixture was subjected to chromatography on silica gel (eluent: benzene–hexane). The crude *O*-alkenyl *N*-benzoyl-*N*-phenylthiocarbamates were purified by distillation or recrystallization from chloroform–hexane.

***O*-Allyl *N*-phenylthiocarbamate 1a.** Yield 85%; mp 65 °C; $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 277 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 20 000); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3350, 3190 and 1615; δ_{H} 5.1 (2 H, br, 1- H_2), 5.29 (1 H, dd, *J* 10.5 and 1.2, 3-H), 5.38 (1 H, d, *J* 17.1, 3-H), 6.0–6.1 (1 H, m, 2-H), 7.2–7.6 (5 H, m, Ph) and 8.8 (1 H, br, NH); δ_{C} 72.9 (t, C-1), 119.1 (t, C-3), 121.7 (d, Ph), 125.5 (d, Ph), 129.0 (d, Ph), 131.3 (d, C-2), 136.9 (s, Ph) and 188.2 (s, C=S) [Found: *m/z* (FAB), 194.0640. Calc. for $\text{C}_{10}\text{H}_{14}\text{NOS}$: (MH^+), 194.0640].

***O*-(2-Methylprop-2-enyl) *N*-phenylthiocarbamate 1b.** Yield 83%; bp 76 °C/2 mmHg; $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 278 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 11 100); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3360, 3190 and 1620; δ_{H} 1.80 (3 H, s, 2-Me), 4.98 (2 H, s, 1- H_2), 5.03 (2 H, s, 3- H_2), 7.2–7.4 (5 H, m, Ph) and 8.6 (1 H, br, NH); δ_{C} 19.7 (q, 2-Me), 75.8 (t, C-1), 114.0 (t, C-3), 121.9 (d, Ph), 125.6 (d, Ph), 129.1 (d, Ph), 136.9 (s, Ph), 139.2 (s, C-2) and 188.5 (s, C=S) [Found: *m/z* (FAB), 208.0798. Calc. for $\text{C}_{11}\text{H}_{14}\text{NOS}$: (MH^+), 208.0796].

***O*-But-2-enyl *N*-phenylthiocarbamate 1c.** Yield 92%; mp 92 °C; $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 279 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 20 500); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3350 and 3150; δ_{H} 1.75 (3 H, dd, *J* 6.3 and 0.8, 3-Me), 5.02 (2 H, br, 1- H_2), 5.7 (1 H, m, 3-H), 5.9 (1 H, m, 2-H), 7.2–7.6 (5 H, m, Ph) and 8.74 (1 H, br, NH); δ_{C} 17.8 (q, 3-Me), 73.3 (t, C-1), 121.5 (d, Ph), 124.3 (d, C-3), 125.3 (d, Ph), 129.0 (d, Ph), 132.5 (d, C-2), 137.1 (s, Ph) and 188.3 (s, C=S) [Found: *m/z* (FAB), 208.0791. Calc. for $\text{C}_{11}\text{H}_{14}\text{NOS}$: (MH^+), 208.0796].

***O*-Allyl *N*-benzoyl-*N*-phenylthiocarbamate 1d.** Yield 76%; mp 38 °C; $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 243 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 15 100) and 278 (10 700); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1680; δ_{H} 1.38 (3 H, s, 2-Me), 4.7–4.8 (2 H, m, 1- H_2), 5.0–5.1 (2 H, m, 3- H_2), 5.4–5.5 (1 H, m, 2-H) and 7.3–7.9 (10 H, m, Ph \times 2); δ_{C} 72.8 (q, C-1), 119.3 (t, C-3), 128.2 (d, Ph), 128.4 (d, Ph), 128.7 (d, Ph), 129.4 (d, Ph), 130.1 (d, C-2), 132.7 (d, Ph), 135.3 (s, Ph), 141.2 (s, Ph), 171.8 (s, C=O) and 191.7 (s, C=S) [Found: *m/z* (FAB), 298.0900. Calc. for $\text{C}_{17}\text{H}_{16}\text{NO}_2\text{S}$: (MH^+), 298.0902].

***O*-(2-Methylprop-2-enyl) *N*-benzoyl-*N*-phenylthiocarbamate 1e.** Yield 80%; mp 60 °C; $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 229 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 14 800) and 240 (14 700); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1690; δ_{H} 1.38 (3 H, s, 2-Me), 4.7 (3 H, m, 1- H_2 and 3-H), 4.8 (1 H, m, 3-H) and 7.3–7.9 (10 H, m, Ph \times 2); δ_{C} 19.2 (q, 2-Me), 76.0 (t, C-1), 114.5 (t, C-3), 128.2 (d, Ph), 128.3 (d, Ph), 128.8 (d, Ph), 129.0 (d, Ph), 129.4 (d, Ph), 132.9 (d, Ph), 135.0 (s, Ph), 138.3 (s, Ph), 141.2 (s, C-2), 171.8 (s, C=O) and 191.7 (s, C=S) [Found: *m/z* (FAB), 312.1059. Calc. for $\text{C}_{18}\text{H}_{18}\text{NO}_2\text{S}$: (MH^+), 312.1058].

***O*-Benzyl *N*-phenylthiocarbamate 4a.** Yield 81%; mp 74 °C; $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 278 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 20 200); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3360 and 2950; δ_{H} 5.63 (2 H, s, OCH_2), 7.1–7.6 (10 H, m, Ph \times 2) and 8.78 (1 H, s, NH); δ_{C} 74.0 (t, OC), 121.6 (d, Ph), 125.4 (d, Ph), 128.2 (d, Ph), 128.4 (d, Ph), 128.6 (d, Ph), 129.0 (d, Ph), 135.0 (s, Ph), 136.9 (s, Ph) and 188.2 (s, C=S) [Found: *m/z* (FAB), 244.0802. Calc. for $\text{C}_{14}\text{H}_{14}\text{NOS}$: (MH^+), 244.0796].

***O*-Methyl *N*-phenylthiocarbamate 4b.** Yield 93%; mp 83 °C; $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 277 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 20 200); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3440, 3180 and 2930; δ_{H} 4.13 (3 H, s, OMe), 7.2–7.5 (5 H, m, Ph) and 8.93 (1 H, br, NH); δ_{C} 58.7 (q, Me), 121.7 (d, Ph), 125.5 (d, Ph), 129.0 (d, Ph), 136.9 (s, Ph) and 189.4 (s, C=S) [Found: *m/z* (FAB), 168.0488. Calc. for $\text{C}_8\text{H}_{10}\text{NOS}$: (MH^+), 168.0483].

O-But-3-enyl N-phenylthiocarbamate 6a. Yield 80%; mp 35 °C; $\lambda_{\max}(\text{C}_6\text{H}_{12})/\text{nm}$ 279 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 21 000); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3380, 3190 and 1615; δ_{H} 2.5–2.6 (2 H, m, 2-H₂), 4.6 (2 H, br, 1-H₂), 5.1–5.2 (2 H, m, 4-H₂), 5.8–5.9 (1 H, m, 3-H), 7.2–7.4 (5 H, m, Ph) and 8.6 (1 H, br, NH); δ_{C} 32.9 (t, C-2), 71.8 (t, C-1), 117.6 (t, C-4), 121.5 (d, Ph), 125.3 (d, Ph), 128.9 (d, Ph), 133.8 (d, C-3), 136.9 (s, Ph) and 188.6 (s, C=S) [Found: m/z (FAB), 208.0796. Calc. for C₁₁H₁₄NOS: ($M\text{H}^+$), 208.0796].

O-(3-Methylbut-3-enyl) N-phenylthiocarbamate 6b. Yield 78%; mp 40 °C; $\lambda_{\max}(\text{C}_6\text{H}_{12})/\text{nm}$ 278 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 19 000); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3360, 3190 and 1620; δ_{H} 1.78 (3 H, s, 3-Me), 2.50 (2 H, t, J 6.6, 2-H₂), 4.7 (2 H, br, 1-H₂), 4.80 (1 H, s, 4-H), 4.85 (1 H, s, 4-H), 7.2–7.3 (5 H, m, Ph) and 8.7 (1 H, br, NH); δ_{C} 22.3 (q, 3-Me), 36.5 (t, C-2), 70.8 (t, C-1), 112.7 (t, C-4), 121.6 (d, Ph), 125.3 (d, Ph), 128.9 (d, Ph), 137.0 (s, Ph), 141.3 (s, C-3) and 188.5 (s, C=S) [Found: m/z (FAB), 222.0954. Calc. for C₁₂H₁₆NOS: ($M\text{H}^+$), 222.0953].

O-[(Z)-Hex-3-enyl] N-phenylthiocarbamate 6c. Yield 75%; mp 46 °C; $\lambda_{\max}(\text{C}_6\text{H}_{12})/\text{nm}$ 279 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 20 900); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3370, 3190 and 1620; δ_{H} 0.96 (3 H, t, J 7.6, 6-H₂), 2.0–2.1 (2 H, m, 5-H₂), 2.54 (2 H, dd, J 13.5 and 6.6, 2-H₂), 4.7 (2 H, br, 1-H₂), 5.3–5.4 (1 H, m, 4-H), 5.5–5.6 (1 H, m, 3-H), 7.2–7.4 (m, 5 H, Ph) and 8.5 (1 H, br, NH); δ_{C} 14.1 (q, C-6), 20.6 (t, C-5), 26.6 (t, C-2), 72.4 (t, C-1), 121.4 (d, C-4), 123.5 (d, Ph), 125.3 (d, Ph), 129.0 (d, Ph), 134.8 (d, C-3), 137.1 (s, Ph) and 188.7 (s, C=S) [Found: m/z (FAB), 236.1109. Calc. for C₁₃H₁₈NOS: ($M\text{H}^+$), 236.1109].

O-But-3-enyl N-benzoyl-N-phenylthiocarbamate 6d. Yield 72%; bp 77 °C/1 mmHg; $\lambda_{\max}(\text{C}_6\text{H}_{12})/\text{nm}$ 240 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 13 900) and 278 (7100); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1680; δ_{H} 2.01 (2 H, ddt, J 13.5, 6.9 and 1.3, 2-H₂), 4.29 (2 H, t, J 6.9, 1-H₂), 4.8–4.9 (1 H, m, 4-H), 4.92 (1 H, d, J 1.3, 4-H), 5.3–5.5 (1 H, m, 3-H) and 7.3–7.9 (10 H, m, Ph \times 2); δ_{C} 32.0 (t, C-2), 71.7 (t, C-1), 117.4 (t, C-4), 128.3 (d, Ph \times 2), 128.7 (d, Ph), 129.4 (d, Ph), 132.7 (d, Ph), 133.1 (d, C-3), 135.4 (s, Ph), 141.2 (s, Ph), 171.9 (s, C=O) and 192.1 (s, C=S) [Found: m/z (FAB), 312.1051. Calc. for C₁₈H₁₈NO₂S: ($M\text{H}^+$), 312.1058].

O-(3-Methylbut-3-enyl) N-benzoyl-N-phenylthiocarbamate 6e. Yield 78%; bp 98 °C/1 mmHg; $\lambda_{\max}(\text{C}_6\text{H}_{12})/\text{nm}$ 241 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 15 400) and 278 (9460); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1670; δ_{H} 1.57 (3 H, s, 3-Me), 1.94 (2 H, t, J 6.9, 2-H₂), 4.35 (2 H, t, J 6.9, 1-H₂), 4.50 (1 H, s, 4-H), 4.67 (1 H, s, 4-H) and 7.3–8.2 (10 H, m, Ph \times 2); δ_{C} 22.2 (q, 3-Me), 35.5 (t, C-2), 70.7 (t, C-1), 112.6 (t, C-4), 128.2 (d, Ph), 128.3 (d, Ph), 128.7 (d, Ph), 129.4 (d, Ph), 130.5 (d, Ph), 132.6 (d, Ph), 135.4 (s, Ph), 140.6 (s, C-3), 141.1 (s, Ph), 171.9 (s, C=O) and 192.0 (s, C=S) [Found: m/z (FAB), 326.1214. Calc. for C₁₉H₂₀NO₂S: ($M\text{H}^+$), 326.1215].

O-[(Z)-Hex-3-enyl] N-benzoyl-N-phenylthiocarbamate 6f. Yield 80%; bp 110 °C/1 mmHg; $\lambda_{\max}(\text{C}_6\text{H}_{12})/\text{nm}$ 242 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 13 000) and 277 (9970); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1680; δ_{H} 0.90 (3 H, t, J 7.5, 6-H₂), 1.8–1.9 (2 H, m, 5-H₂), 2.0 (2 H, m, 2-H₂), 4.22 (2 H, t, J 7.0, 1-H₂), 4.9 (m, 1 H, 4-H), 5.3–5.4 (1 H, m, 3-H) and 7.2–7.9 (10 H, m, Ph \times 2); δ_{C} 14.1 (q, C-6), 20.4 (t, C-5), 25.6 (t, C-2), 72.1 (t, C-1), 122.7 (d, C-4), 128.2 (d, Ph), 128.3 (d, Ph), 128.6 (d, Ph), 128.7 (d, Ph), 129.4 (d, Ph), 134.6 (d, C-3), 135.5 (s, Ph), 141.3 (s, Ph), 171.9 (s, C=O) and 192.2 (s, C=S) [Found: m/z (FAB), 340.1375. Calc. for C₂₀H₂₂NO₂S: ($M\text{H}^+$), 340.1371].

General Procedure for the Photolysis of the O-Alkenyl Thiocarbamates 1a–e, 4a, b and 6a–f.—A benzene solution of thiocarbamate (0.02 mol dm⁻³) in a Pyrex vessel under Ar was irradiated at 15 °C with the UV light from a 1 kW high pressure mercury lamp until the starting material had almost disappeared. The residue obtained by concentration of the reaction mixture was subjected to flash chromatography (eluent: benzene–hexane). The crystalline products were recrystallized from chloroform–hexane.

S-Allyl N-phenylthiocarbamate 2a. Mp 60 °C; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3360 and 1670; δ_{H} 3.6 (2 H, m, 1-H₂), 5.1 (1 H, m, 3-H), 5.3 (1 H, m, 3-H), 5.8–6.0 (1 H, m, 2-H) and 7.1–7.4 (6 H, m, Ph and NH); δ_{C} 33.1 (t, C-1), 117.9 (t, C-3), 119.9 (d, Ph), 124.5 (d, Ph), 129.1 (d, Ph), 133.6 (d, C-2), 137.6 (s, Ph) and 165.2 (s, C=O) [Found: m/z (FAB), 194.0642. Calc. for C₁₀H₁₂NOS: ($M\text{H}^+$), 194.0640].

S-(2-Methylprop-2-enyl) N-phenylthiocarbamate 2b. Mp 39 °C; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3380 and 1670; δ_{H} 1.82 (3 H, dd, J 0.8 and 1.4, 2-Me), 3.65 (2 H, m, 1-H₂), 4.87 (1 H, m, 3-H), 5.02 (1 H, m, 3-H) and 7.1–7.4 (6 H, m, Ph and NH); δ_{C} 21.1 (q, 2-Me), 37.2 (t, C-1), 114.2 (t, C-3), 119.7 (d, Ph), 124.5 (d, Ph), 129.1 (d, Ph), 137.7 (s, Ph), 141.1 (s, C-2) and 165.4 (s, C=O) [Found: m/z (FAB), 208.0800. Calc. for C₁₁H₁₄NOS: ($M\text{H}^+$), 208.0796].

S-But-2-enyl N-phenylthiocarbamate 2c. Mp 48 °C; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3360 and 1630; δ_{H} 1.68 (3 H, ddd, J 6.6, 2.7 and 1.1, 3-Me), 3.59 (2 H, dt, J 7.2 and 1.1, 1-H₂), 5.5–5.6 (1 H, m, 3-H), 5.7 (m, 1 H, 2-H) and 7.1–7.4 (6 H, m, Ph and NH); δ_{C} 17.8 (q, 3-Me), 32.5 (t, C-1), 119.8 (d, Ph), 125.2 (d, Ph), 126.2 (d, C-3), 129.1 (d, Ph), 129.3 (d, C-2), 137.7 (s, Ph) and 165.5 (s, C=O) [Found: m/z (FAB), 208.0796. Calc. for C₁₁H₁₄NOS: ($M\text{H}^+$), 208.0796].

S-Allyl N-benzoyl-N-phenylthiocarbamate 2d. Bp 91 °C/1 mmHg; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1760 and 1660; δ_{H} 3.5 (2 H, m, 1-H₂), 5.1 (1 H, m, 3-H₂), 5.2 (1 H, m, 3-H₂), 5.8 (m, 1 H, 2-H) and 7.3–7.7 (10 H, m, Ph \times 2); δ_{C} 34.3 (t, C-1), 128.2 (d, Ph), 128.6 (d, Ph), 129.4 (d, Ph), 123.0 (d, Ph), 131.9 (d, Ph), 132.7 (d, Ph), 134.9 (s, Ph), 137.4 (s, Ph), 171.3 (s, C=O) and 171.5 (s, C=O) [Found: m/z (FAB), 298.0896. Calc. for C₁₇H₁₆O₂NS: ($M\text{H}^+$), 298.0902].

S-(2-Methylprop-2-enyl) N-benzoyl-N-phenylthiocarbamate 2e. Mp 61 °C; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1730 and 1650; δ_{H} 1.7–1.8 (3 H, m, 2-Me), 3.51 (2 H, d, J 1.0, 1-H₂), 4.8 (m, 1 H, 3-H), 4.92 (1 H, d, J 0.7, 3-H) and 7.3–7.7 (10 H, m, Ph \times 2); δ_{C} 21.3 (q, 2-Me), 38.2 (t, C-1), 114.5 (t, C-3), 128.2 (d, Ph), 128.5 (d, Ph), 129.3 (d, Ph), 129.4 (d, Ph), 130.0 (d, Ph), 131.9 (d, Ph), 134.9 (s, Ph), 137.5 (s, Ph), 140.2 (s, C-2), 171.3 (s, C=O) and 171.8 (s, C=O) [Found: m/z (FAB), 312.1052. Calc. for C₁₈H₁₈O₂NS: ($M\text{H}^+$), 312.1058].

S-Benzyl N-phenylthiocarbamate 5a. Mp 88 °C; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3390 and 1670; δ_{H} 4.22 (2 H, s, S-CH₂) and 7.1–7.4 (11 H, m, Ph \times 2 and NH); δ_{C} 34.5 (t, SC), 119.9 (d, Ph), 124.6 (d, Ph), 127.3 (d, Ph), 128.6 (d, Ph), 128.8 (d, Ph), 129.1 (d, Ph), 137.6 (s, Ph), 137.9 (s, Ph) and 165.2 (s, C=O) [Found: m/z (FAB), 244.0798. Calc. for C₁₄H₁₄NOS: ($M\text{H}^+$), 244.0796].

2-Phenylimino-3-sulfanylmethylloxolane 7a. Bp 72 °C/1 mmHg; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2450 and 1680; δ_{H} 1.8 (1 H, br, SH, D₂O exchangeable), 2.1–2.2 (1 H, m, 4-H), 2.3–2.4 (1 H, m, 4-H), 2.9–3.0 (2 H, m, SCH₂), 3.0–3.1 (1 H, m, 3-H), 4.17 (1 H, td, J 8.8 and 6.9, 5-H), 4.34 (1 H, td, J 8.8 and 3.3, 5-H) and 7.0–7.1 (3 H, m, Ph) and 7.2–7.3 (2 H, m, Ph); δ_{C} 26.1 (t, C-4), 27.6 (t, SC), 43.3 (d, C-3), 69.0 (t, C-5), 122.4 (d, Ph), 123.7 (d, Ph), 128.6 (d, Ph), 146.8 (s, Ph) and 163.1 (s, C=N) [Found: m/z (FAB), 208.0801. Calc. for C₁₁H₁₄NOS: ($M\text{H}^+$), 208.0796].

3-Methyl-2-phenylimino-3-sulfanylmethylloxolane 7b. Bp 63 °C/1 mmHg; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2390 and 1680; δ_{H} 1.40 (3 H, s, 3-Me), 1.64 (1 H, dd, J 9.9 and 7.9, SH, D₂O exchangeable), 1.91 (1 H, ddd, J 12.6, 7.1 and 4.0, 4-H), 2.47 (1 H, td, J 12.6 and 8.6, 4-H), 2.67 (1 H, dd, J 13.9 and 9.9, SCH), 3.00 (1 H, dd, J 13.9 and 7.9, SCH), 4.21 (1 H, td, J 8.6 and 7.1, 5-H), 4.29 (1 H, td, J 8.6 and 4.0, 5-H), 7.0–7.1 (m, 2 H, Ph) and 7.2–7.3 (m, 2 H, Ph); δ_{C} 24.0 (q, 3-Me), 33.2 (t, C-4), 33.5 (t, SC), 45.5 (s, C-3), 67.5 (t, C-5), 122.3 (d, Ph), 123.6 (d, Ph), 128.5 (d, Ph), 146.9 (s, Ph) and 166.4 (s, C=N) [Found: m/z (FAB), 222.0958. Calc. for C₁₂H₁₆NOS: ($M\text{H}^+$), 222.0953].

2-Phenylimino-3-(1-sulfanylpropyl)oxolane 7c. Bp. 85 °C/1 mmHg; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1680; δ_{H} 1.11 (3 H, t, J 7.4, 3'-H₃),

1.6–1.7 (2 H, m, 2'-H₂), 1.68 (1 H, d, *J* 6.3, SH, D₂O exchangeable), 2.1–2.2 (1 H, m, 4-H), 2.3–2.4 (1 H, m, 4-H), 3.16 (1 H, td, *J* 9.4 and 3.3, 3-H), 3.5–3.6 (1 H, m, 1'-H), 4.1–4.2 (1 H, m, 5-H), 4.38 (1 H, td, *J* 8.8 and 3.0, 5-H), 7.0–7.1 (2 H, m, Ph) and 7.2–7.3 (2 H, m, Ph); δ_{C} 12.3 (q, C-3'), 23.0 (t, C-2'), 29.2 (t, C-4), 43.2 (d, C-3), 46.5 (d, C-2'), 69.5 (t, C-5), 122.4 (d, Ph), 123.6 (d, Ph), 128.6 (d, Ph), 147.1 (s, Ph) and 163.9 (s, C=N) [Found: *m/z* (FAB), 236.1115. Calc. for C₁₃H₁₈NOS: (MH⁺), 236.1109].

3-(Benzoylsulfanylmethyl)-2-phenyliminooxolane **7d**. Bp 109 °C/1 mmHg; ν_{max} (CHCl₃)/cm⁻¹ 1680 and 1650; δ_{H} 2.0–2.1 (1 H, m, 4-H), 2.3–2.4 (1 H, m, 4-H), 3.2–3.3 (1 H, m, 3-H), 3.45 (1 H, dd, *J* 13.7 and 7.4, SCH), 3.72 (1 H, dd, *J* 13.7 and 4.1, SCH), 4.1–4.2 (1 H, m, 5-H), 4.32 (1 H, td, *J* 8.5 and 3.0, 5-H), 7.0–7.1 (2 H, m, Ph), 7.2–7.3 (2 H, m, Ph), 7.4–7.5 (m, 2 H, Ph), 7.5–7.6 (1 H, m, Ph) and 8.0 (2 H, m, Ph); δ_{C} 28.1 (t, C-4), 29.7 (t, SC), 41.3 (d, C-3), 69.0 (t, C-5), 122.4 (d, Ph), 123.7 (d, Ph), 127.3 (d, Ph), 128.5 (d, Ph), 128.6 (d, Ph), 133.5 (d, Ph), 136.7 (s, Ph), 146.8 (s, Ph), 163.2 (s, C=N) and 191.6 (s, C=O) [Found: *m/z* (FAB), 312.1066. Calc. for C₁₈H₁₈NO₂S: (MH⁺), 312.1058].

3-(Benzoylsulfanylmethyl)-3-methyl-2-phenyliminooxolane **7e**. Bp 103 °C/1 mmHg; ν_{max} (CHCl₃)/cm⁻¹ 1680 and 1650; δ_{H} 1.48 (3 H, s, 3-Me), 1.95 (1 H, ddd, *J* 12.8, 7.0 and 4.8, 4-H), 2.23 (1 H, dt, *J* 12.8 and 8.0, 4-H), 2.53 (2 H, s, SCH₂), 4.2 (1 H, m, 5-H), 4.31 (1 H, td, *J* 8.2 and 4.8, 5-H), 7.0–7.1 (2 H, m, Ph), 7.2–7.3 (2 H, m, Ph), 7.4–7.5 (2 H, m, Ph), 7.5–7.6 (1 H, m, Ph) and 8.0 (2 H, m, Ph); δ_{C} 24.2 (q, 3-Me), 33.9 (t, C-4), 36.3 (t, SC), 44.8 (s, C-3), 67.7 (t, C-5), 122.3 (d, Ph), 123.6 (d, Ph), 127.3 (d, Ph), 128.5 (d, Ph), 128.6 (d, Ph), 133.5 (d, Ph), 136.7 (s, Ph), 147.0 (s, Ph), 166.3 (s, C=N) and 191.5 (s, C=O) [Found: *m/z* (FAB), 326.1209. Calc. for C₁₉H₂₀NO₂S: (MH⁺), 326.1215].

3-Propylidene-2-phenyliminooxolane **8f**. Bp 84 °C/1 mmHg; ν_{max} (CHCl₃)/cm⁻¹ 1660; δ_{H} 1.12 (3 H, t, *J* 7.5, 3'-H₃), 2.23 (2 H, qd, *J* 7.5 and 6.0, 2'-H₂), 2.8 (2 H, m, 4-H₂), 4.3–4.4 (2 H, m, 5-H₂), 6.7 (1 H, m, 1'-H), 7.0–7.1 (1 H, m, Ph), 7.1–7.2 (2 H, m, Ph) and 7.2–7.3 (2 H, m, Ph); δ_{C} 13.1 (q, C-3'), 23.6 (t, C-2'), 26.2 (t, C-4), 68.2 (t, C-5), 123.0 (d, Ph), 123.5 (d, Ph), 128.6 (d, Ph), 128.7 (s, C-3) and 135.1 (d, C-1'), 147.3 (s, Ph) and 158.8 (s, C=N) [Found: *m/z* (FAB), 202.1230. Calc. for C₁₃H₁₆NO: (MH⁺), 202.1232].

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