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Intramolecular addition of benzylic radicals onto ketenimines. Synthesis of 2-alkylindoles

Mateo Alajarín, Angel Vidal * and María-Mar Ortín
Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, 30100 Murcia, Spain. E-mail: vidal@um.es; Fax: 34 968 364149; Tel: 34 968 367418

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The inter- and intramolecular addition of free radicals onto ketenimines is studied. All the attempts to add intermolecularly several silicon, oxygen or carbon centered radicals to *N*-(4-methylphenyl)-*C*,*C*-diphenyl ketenimine were unsuccessful. In contrast, the intramolecular addition of benzylic radicals, generated from xanthates, onto the central carbon of a ketenimine function with its *N* atom linked to the *ortho* position of the aromatic ring occurred under a variety of reaction conditions. These intramolecular cyclizations provide a novel radical-mediated synthesis of 2-alkylindoles.

Introduction

In the field of modern organic synthesis, free radical chemistry[1] is gaining considerable importance and getting its place alongside the more familiar ionic chemistry, due to its growing versatility, predictability and functional group tolerance. In recent years, radical chemistry has become a powerful and standard strategy in the total synthesis of natural products[2] and in the preparation of heterocyclic compounds.[3]

The known chemistry of ketenimines is mainly based on the addition of nucleophiles to their electrophilic *sp*-hybridized carbon atom, and on their participation in pericyclic processes.[4] However, the radical chemistry of ketenimines remains unexplored. To the best of our knowledge no inter or intramolecular free radical additions to ketenimines have been reported. Moreover, the free radical chemistry of heterocumulenes is practically unknown,[5] with the exception of those of ketenes and isothiocyanates which are currently under investigation by the groups of Tidwell[6] and Nanni,[7] respectively.

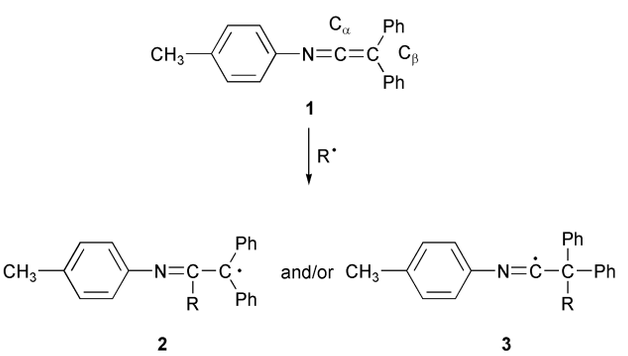
In the last few years, we have been involved in the study of the chemical behaviour of ketenimines. In our hands, these heterocumulenes have been successfully employed in the synthesis of nitrogen-containing heterocycles, *via* their participation in electrocyclic ring closures,[8] intramolecular [2 + 2][9] and [4 + 2][10] cycloadditions, and imino-ene type reactions.[11] Now we have focused our attention on the development of inter- and intramolecular radical processes involving ketenimines as substrates.

We present here our results in the study of the intermolecular addition reactions of different types of free radicals onto ketenimines and those concerning the intramolecular addition of benzylic radicals onto a ketenimine function linked to an *ortho* position on the aromatic ring by means of its nitrogen atom.[12] These intramolecular cyclizations represent a novel methodology for the synthesis of indoles.[13]

Results and discussion

Intermolecular addition of free radicals to ketenimines

Our first try at the radical chemistry of ketenimines was the intermolecular addition of different types of free radicals ($R^{\bullet}$) to the easily available, and stable, *N*-(4-methylphenyl)-*C*,*C*-diphenyl ketenimine **1**,[14] with the aim of establishing the feasibility of these intermolecular processes and their regioselectivity. On the basis of the results of Tidwell and co-workers on the radical reactions of ketenes,[6] it is conceivable that radicals $R^{\bullet}$ could add initially to carbon atoms C_α or C_β of the ketenimine **1** to give either a *tert*-alkyl radical **2** or an imidoyl radical **3** (Scheme 1). Afterwards, radicals **2** and **3**, depending on the reaction conditions, could undergo reduction, dimerization or be captured by other species present in the reaction medium.



Scheme 1 Presumed main paths for the intermolecular addition of free radicals to ketenimines.

The ionic chemistry of ketenimines involves the attack of nucleophiles at the C_α carbon atom.[4] As it occurs for ketenes, it may be expected that the free radical chemistry of ketenimines parallels their ionic chemistry and thereby the tendency for nucleophilic radicals to attack at C_α. The regiochemistry of radical additions to ketenimines must also be influenced by the stability of the radical resulting from the initial addition. Thus, the addition of radicals to ketenimines should preferentially give type **2** alkyl radicals (*versus* the less stable sp^2 carbon centered type **3** radicals), especially if the stability of radical **2** is adequately enhanced by placing stabilizing substituents on the sp^3 carbon atom, as is the case shown in Scheme 1.

Unfortunately, all the attempts to add several silicon, oxygen or carbon-centered radicals to ketenimine **1** under reaction conditions very similar to those in which these classes of radicals react with compounds containing C=C or C≡C bonds were unsucessful. In these reactions ketenimine **1** was recovered unaltered or gave rise to complex reaction mixtures that we could not resolve.

Experiments with the silyl radical $[(CH_3)_3Si]_3Si^{\bullet}$, generated by reacting tris(trimethylsilyl)silane and AIBN in benzene or toluene at reflux temperature,[15] did not provide evidence for

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intermolecular attack on ketenimine **1**. No reaction was observed even after we added a stoichiometric excess of tris(trimethylsilyl)silane/AIBN. Similarly, from the reaction of ketenimine **1** with four equivalents of the commercially available oxygen centered radical TEMPO[16] (2,2,6,6-tetramethyl-1-piperidinyloxy free radical), in dichloromethane at room temperature, compound **1** was recovered. In sharp contrast, when we carried out the reaction of **1** with TEMPO in benzene or toluene at reflux temperature we only obtained complex reaction mixtures.

As already mentioned, the reaction of ketenimine **1** with carbon radicals was also explored. For this purpose, amongst all the reported methods for producing carbon radicals we selected those involving (a) the reaction of xanthates with organic peroxides as radical initiators,[17] and (b) the reaction of alkyl phenyl selenides with the system tris(trimethylsilyl)silane/AIBN.[18] Using the xanthate-based methodology we did not observe a reaction when we added only a catalytic amount of the peroxide initiator to the reaction mixture. In fact, the radical precursor was totally consumed only when a stoichiometric amount of peroxide was added. In these cases complex reaction mixtures were formed in which none of the expected radical addition products could be detected. Finally, the addition of carbon radicals to ketenimine **1** also failed when this heterocumulenic compound was submitted to reaction with several secondary alkyl or benzyl phenyl selenides in the presence of an excess of tris(trimethylsilyl)silane/AIBN.

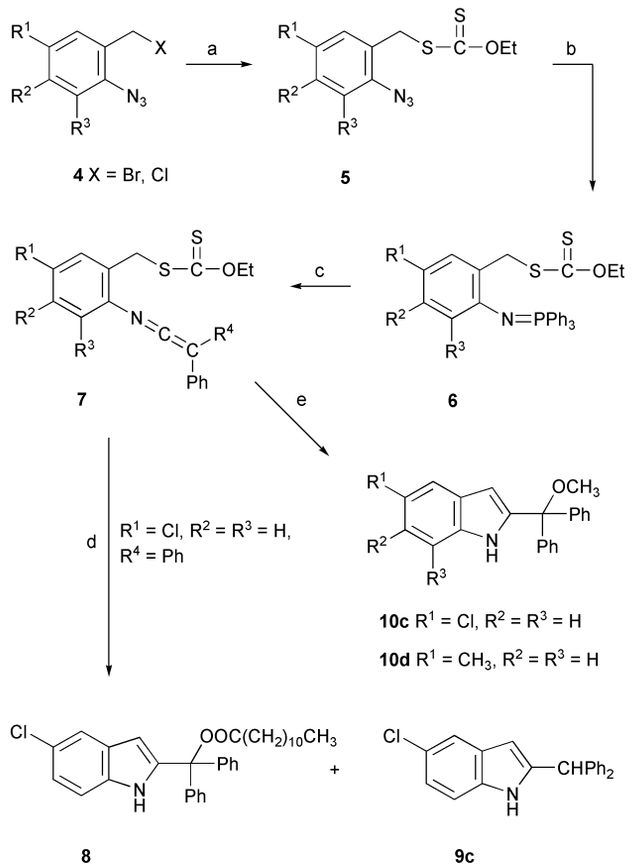
Although we did not obtain any successful results in our attempts to add free radicals to ketenimines intermolecularly, this study gave us a background of radical reaction conditions under which a ketenimine function could survive, which was actually very useful in the study of the intramolecular processes.

Intramolecular addition of benzylic radicals onto ketenimines

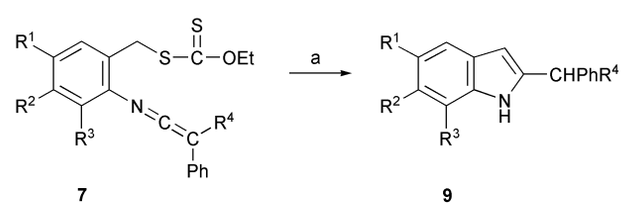
We reasoned that the entropic assistance inherent to intramolecular reactions would hopefully allow us to achieve the intramolecular addition of radicals to ketenimines. To that end, ketenimines **7** (Scheme 2) were specifically designed for generating benzylic radicals which could undergo a favoured *5-exo-dig* cyclization onto the central carbon of the ketenimine function. In compounds **7** two substituents are placed on the terminal carbon atom of the ketenimine function in order to obtain stabilized tertiary radicals in the cyclization step, thus making that cyclization a more favourable process. Compounds **7** bear a xanthate group from which the benzylic radical could be generated under mild reaction conditions. Moreover, the xanthate group is compatible with our well-established methodology for the preparation of ketenimines, that is, the aza-Wittig reaction of phosphazenes and ketenes.[8–11]

Ketenimines **7** were prepared in high overall yields from the 2-azidobenzyl bromides or chlorides **4** in three steps (Scheme 2). The substitution of the bromine or chlorine atom in compounds **4** by the xanthate group to provide xanthates **5** was carried out by reaction with the commercially available salt KSC(S)OEt, in acetone at room temperature. Staudinger treatment[19] of the azidoxanthates **5** with triphenylphosphane, in diethyl ether solution at room temperature, yielded the triphenylphosphazenes **6**. Reaction of the triphenylphosphazenes **6** with 1 equivalent of methyl phenyl ketene or diphenyl ketene, in dichloromethane at room temperature for a short period of time, gave ketenimines **7**. Compounds **7** were purified by column chromatography on silica gel and were fully characterized (see experimental section). Their IR spectra showed strong absorptions around 2000 cm^{-1} attributable to the N=C=C grouping.

Radical cyclization of ketenimines **7** was explored under different conditions (Schemes 2 and 3). Gradual addition of a stoichiometric excess (1.5 eq.) of lauroyl peroxide as radical



Scheme 2 *Reagents and conditions*: (a) KSC(S)OEt, acetone, rt, 1 h; (b) PPh_3, diethyl ether, rt, 6 h; (c) $PhR^4C{=}C{=}O$, dichloromethane, rt, 30 min; (d) lauroyl peroxide (1.5 eq.), cyclohexane, reflux, 30 h; (e) lauroyl peroxide (1.2 eq.), methanol/1,2-dichloroethane, reflux, 24 h.



Scheme 3 *Reagents and conditions*: (a) *t*-butyl peroxide (1.2 eq.), chlorobenzene, reflux, 24 h.

initiator to a 0.01 M solution of ketenimine **7c** (R^1 = Cl, R^2 = R^3 = H, R^4 = Ph) in boiling cyclohexane produced indole **8**, which incorporates the lauroyloxy fragment, in 38% yield, along with a small amount (4%) of the reduced indole **9c**. The reaction initiated by lauroyl peroxide and conducted in a mixture of methanol/1,2-dichloroethane (1 : 3; v/v) led to 2-(α-methoxy-α,α-diphenyl)methylindole **10c** in 43% yield.[20] When a stoichiometric amount of *t*-butyl peroxide was added portionwise to a 0.01 M solution of ketenimine **7c** in boiling chlorobenzene, 5-chloro-2-diphenylmethylindole **9c** was obtained in 60% yield, as the only product which could be isolated from the reaction mixture.

Using methanol/1,2-dichloroethane as reaction medium the cyclization of ketenimine **7d** (R^1 = CH_3, R^2 = R^3 = H, R^4 = Ph) was also achieved to give **10d** (34%) (Scheme 2).[20] Cyclization of ketenimines **7a**,**b**,**d**–**h** under the *t*-butyl peroxide/chlorobenzene conditions furnished further examples of 2-substituted indoles **9** in moderate yields (Scheme 3) (Table 1).

The structural characterization of indoles **8**, **9** and **10** relies on their analytical and spectroscopic data.[21] In this respect, the IR spectrum of indole **8** shows a strong absorption at 1706 cm^{-1} corresponding to the C=O vibration. In the ^1H NMR spectrum of this compound the indolic NH appears as a broad singlet at

Table 1 2-substituted indoles **9** from ketenimines **7**

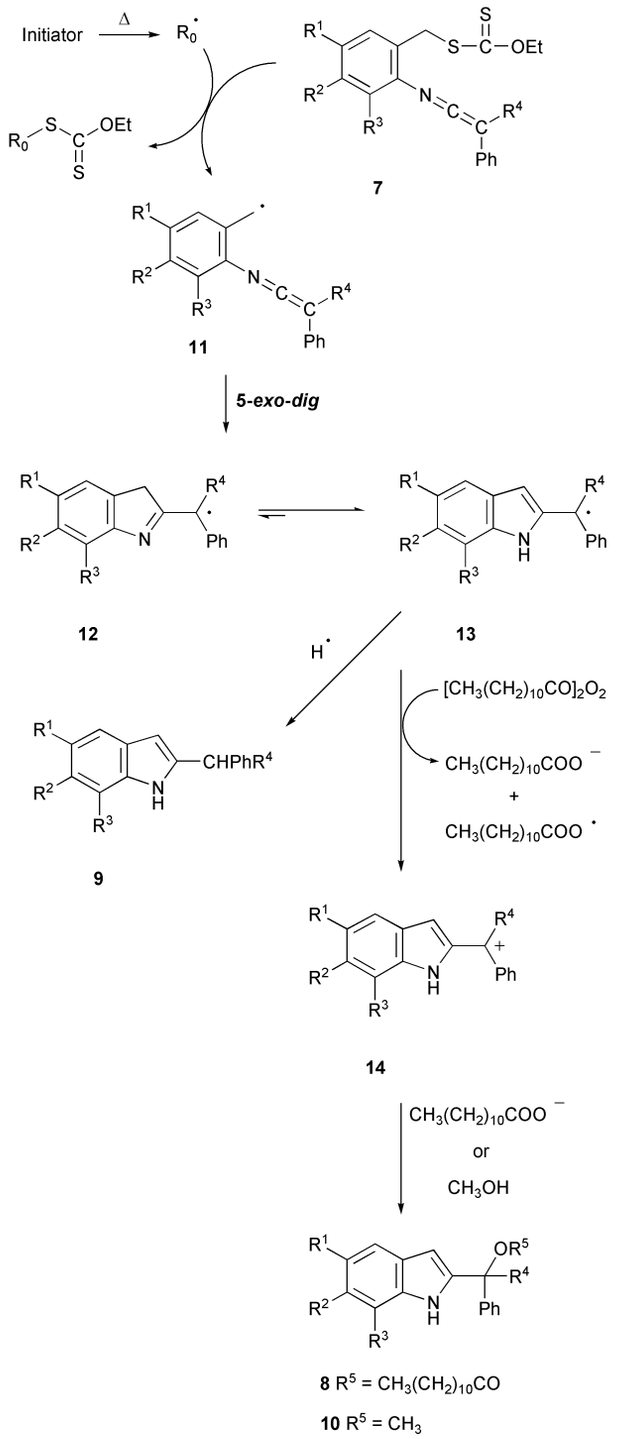
Compound	R^1	R^2	R^3	R^4	Yield (%)
9a	H	H	H	Ph	50
9b	Br	H	H	Ph	24
9c	Cl	H	H	Ph	60
9d	CH_3	H	H	Ph	47
9e	H	NO_2	H	Ph	64
9f	H	H	CH_3	Ph	60
9g	C_6H_4		H	Ph	52
9h	H	H	H	CH_3	44

δ = 8.49, and the C(3)H proton is observed at δ = 6.04. The ^{13}C NMR spectrum shows the signal due to the C=O group at δ = 179.3. The incorporation of the methoxy group on the indoles **10** was demonstrated by the presence in their ^{1}H NMR spectra of a singlet near δ = 3.1, integrating three protons, and the appearance in their ^{13}C NMR spectra of a signal at δ = 52.4. Concerning the structural determination of the indoles **9**, the methine proton of the substituent at C2 resonates as a singlet in their ^{1}H NMR spectra at δ = 6.00–6.42 for compounds **9a**–**g**, or as a quartet at δ = 4.29 for **9h**. The C(3)H proton appears at δ = 6.00–6.42. Their ^{13}C NMR spectra show the signals due to the methine carbon of the mentioned substituent at δ = 39.2–51.4, and that of C3 at δ = 99.6–103.7. The MS and analytical data of indoles **8**, **9** and **10** are in perfect agreement with the proposed structures.

A reasonable mechanism for explaining the conversions **7**⟶**8**, **7**⟶**9** and **7**⟶**10** is shown in Scheme 4. The thermal decomposition of the peroxide initiator produces radical $(R_0)^{\bullet}$, which exchanges the xanthate group with ketenimines **7** giving rise to the expected benzylic radicals **11**, which then undergo a 5-*exo*-*dig* addition of the radical moiety onto the electrophilic central carbon atom of the ketenimine function, followed by a prototropic imine–enamine equilibrium favouring the aromatic indole form **13**. The stabilized tertiary triarylmethyl-type radicals **13** did not react with a new molecule of **7** to sustain the radical chain sequence.[22] Instead they underwent reduction to give indoles **9**, or electron transfer to the lauroyl peroxide to furnish carbocations **14**, which under the reaction conditions were quenched by the carboxylate anion generated in the redox process,[23] to furnish indole **8**, or if methanol was used as solvent, to afford indoles **10**.[23b]

The conversion of ketenimines **7** into the indoles **9** is a reductive process and the hydrogen atom donor toward the intermediate radicals **13** is not obvious.[24] In this respect, we were not able to isolate any product from the crude reaction mixtures that provides us with evidence about which species present in the reaction medium acts as the source of hydrogen atoms. We reasoned that the yield of these reactions might be improved by addition to the reaction mixture of hydrogen donors. With this aim we chose 1,4-cyclohexadiene which is compatible with the ketenimine function. The addition of 5 equivalents of 1,4-cyclohexadiene to the initial reaction mixture of the treatment of ketenimine **7d** with *t*-butyl peroxide led to a cleaner reaction, but the yield of the corresponding indole **9d** did not improve.

Then, we directed our efforts towards obtaining mechanistic insights into the radical conversions here described. Attempts of trapping intermolecularly the benzylic radicals **11** by carrying out the radical cyclization of ketenimines **7** in the presence of an excess of allyl acetate or benzyl acrylate failed. These results prove that the cyclization of radicals **11** is a more favourable path due to the great stability of the tertiary radicals **12** and **13**. We also conducted an experiment aimed at capturing radicals **13**. It is known that *t*-butyl peroxide abstracts hydrogen atoms from substituted toluenes to yield benzylic radicals.[25] Thus we performed the radical cyclization of ketenimine **7d** using *t*-butyl peroxide as radical initiator in boiling *ortho*-xylene[26] pleasantly obtaining the indole **15** in 52% yield. Indole

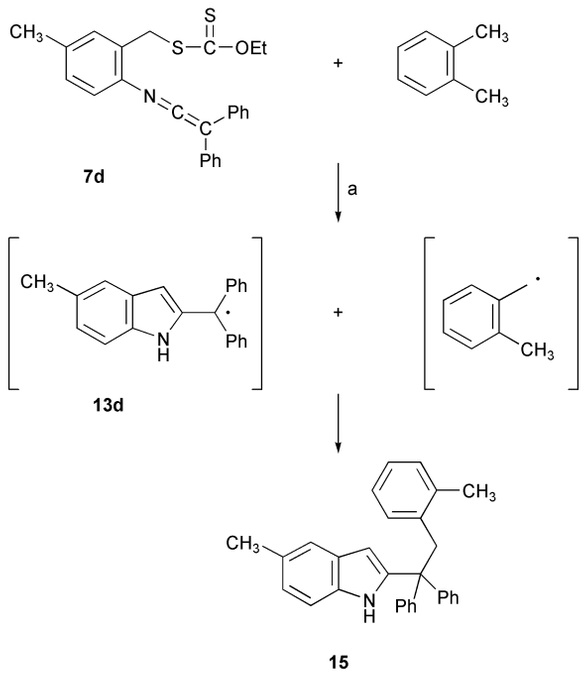


Scheme 4 Proposed mechanism for the conversions **7**⟶**8**, **7**⟶**9** and **7**⟶**10**.

15 should be formed by the coupling of radical **13d** with that arising from the *ortho*-xylene (Scheme 5).

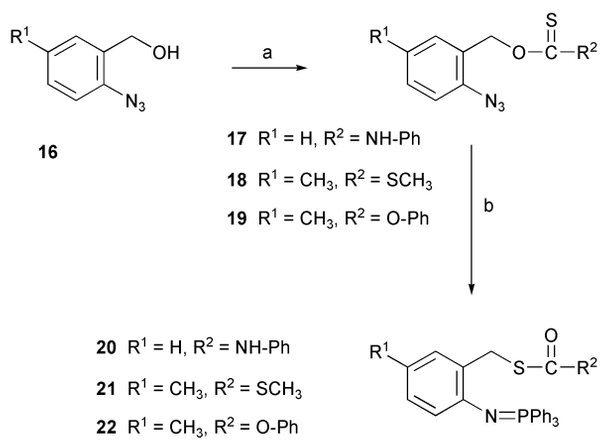
An attractive alternative that we considered for generating the benzylic radicals **11** was the substitution of the *O*-ethyl xanthate group present in the ketenimines **7** by other radical-precursor functional groups, such as *N*-phenylthioxocarbamate, *S*-methyl xanthate and phenylthionocarbonate. The reaction of these new derivatives with the good hydrogen donor tris(trimethylsilyl)silane[18,27] in the presence of AIBN as radical initiator could also provide the desired benzylic radicals **11**, and accordingly the indoles **9**.

The treatment of the azidobenzyl alcohols **16** with phenylisothiocyanate, carbon disulfide/methyl iodide or phenyl chlorothionoformate/DMAP, under standard conditions, yielded the *N*-phenylthioxocarbamate **17**, the *S*-methyl xanthate **18** and the



Scheme 5 *Reagents and conditions*: (a) *t*-butyl peroxide (1.2 eq.), *ortho*-xylene, reflux, 24 h.

phenylthionocarbonate **19**, respectively. The Staudinger reaction of azides **17**–**19** with triphenylphosphane, in diethyl ether solution at room temperature, afforded the triphenylphosphazenes **20**–**22**, in which the benzyl group has experienced an oxygen to sulfur migration (Scheme 6).



Scheme 6 *Reagents and conditions*: (a) Ph–NCS, NaH, tetrahydrofuran, rt, 16 h to give **17**; (a) CS_2, NaH, tetrahydrofuran, rt 2 h and 50 °C 1 h, then CH_3I, 50 °C, 6 h to give **18**; (a) Ph–O–C(S)Cl, DMAP, acetonitrile, rt, 1 h to give **19**; (b) PPh_3, diethyl ether, rt, 6 h.

The determination of the structure of compounds **20**–**22** was mainly based on their ^1H and ^{13}C NMR spectroscopic data. Of particular relevance were the observed chemical shifts for the protons of the benzylic methylene group in their ^1H NMR spectra, and the chemical shifts of the carbon atom of that group in their ^{13}C NMR spectra. In all cases, a notable upfield shift was observed for the nuclei mentioned above when compared with the chemical shifts of the same nuclei in the corresponding azides **17**–**19** (Table 2). These shift differences support that in compounds **20**–**22** the benzyl group is on the sulfur atom. Also in the ^{13}C NMR spectra of the triphenylphosphazenes **20**–**22** the signals that appear at higher δ values have undergone an upfield shift with respect the same signals in the spectra of the azides **17**–**19**, accounting for the presence of a carbonyl instead of a thiocarbonyl group in compounds **20**–**22**.

Table 2 Selected NMR data for compounds **17**–**19** and **20**–**22**

Compound	δ_H CH_2	δ_C CH_2	δ_C C=S	δ_C C=O
17	5.58	69.5[a]	188.1	
18	5.54	70.9	215.6	
19	5.47	71.3	194.9	
20	4.52	33.0		167.6
21	4.52	33.6		191.4
22	4.46	34.7		172.1

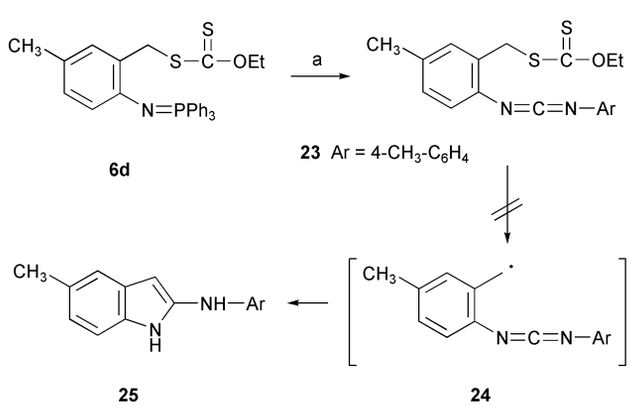
[a] Very broad signal.

The *O*- to *S*- transpositions observed in the formation of triphenylphosphazenes **20**–**22** belong to a known class of reactions. Probably, these compounds are formed *via* a Newman–Kwart [28] or Schönberg [29] rearrangement, but this was unexpected for us given the mild reaction conditions involved in the Staudinger treatment of azides **17**–**19**.

Attempts at intramolecular addition of benzylic radicals onto carbodiimides and isothiocyanates

The success of the radical cyclization of ketenimines **7** led us to study similar reactions of structurally related compounds in which the ketenimine moiety has been substituted by other heterocumulenic functions such as carbodiimide or isothiocyanate.

To test the feasibility of the intramolecular addition of benzylic radicals onto carbodiimides we prepared compound **23** by reaction of triphenylphosphazene **6d** and 4-methylphenylisocyanate (Scheme 7). However, all the attempts at radical cyclization of the xanthate-carbodiimide **23** under similar reaction conditions to those utilized in the cyclization of ketenimines **7** failed and just yielded complex reaction mixtures.

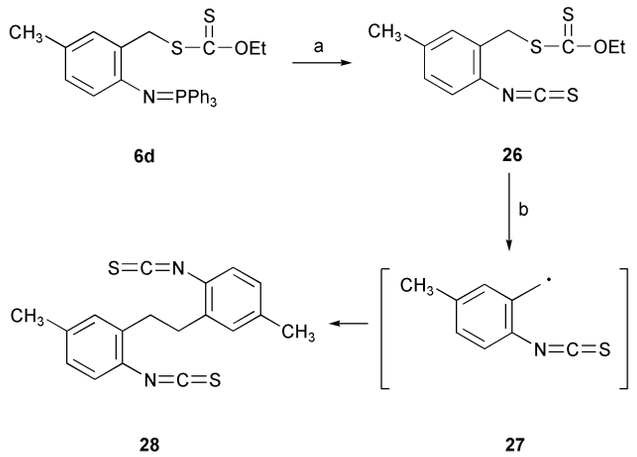


Scheme 7 *Reagents and conditions*: (a) 4-CH_3–C_6H_4–NCO, dichloromethane, rt, 30 min.

The isothiocyanate **26** was easily obtained by reaction of triphenylphosphazene **6d** with carbon disulfide. The addition, in small portions, of a stoichiometric amount of lauroyl peroxide to a solution of isothiocyanate **26** (0.015 M) in boiling cyclohexane did not give any product resulting from the intramolecular cyclization of the intermediate benzylic radical **27**, instead the dimeric bis(isothiocyanate) **28** was obtained in quantitative yield (Scheme 8).

Conclusion

In summary, in this report we have described the difficulties encountered in the intermolecular addition of free radicals to ketenimines and the feasibility of this process in its intramolecular version. We have shown how ketenimines undergo intramolecular addition of free carbon-centered radicals, generated from xanthates, providing a new radical tin-free route to



Scheme 8 *Reagents and conditions*: (a) CS_2, benzene, reflux, 12 h; (b) lauroyl peroxide (1.0 eq.), cyclohexane, reflux, 24 h.

indoles. The success of these cyclizations may be due to the exceptional stability of the radicals resulting from the cyclization step.

Experimental

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC200 or on a Varian Unity 300 and are reported in ppm on the δ scale. *J* values are given in Hz. Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer or on a VG-Autospec spectrometer. Microanalyses were performed on a Carlo Erba EA-1108 instrument.

Materials

2-Azidobenzyl chloride **4a**,[30] 2-azido-5-chlorobenzyl chloride **4c**,[31] 2-azido-5-methylbenzyl chloride **4d**,[32] 2-azido-4-nitrobenzyl bromide **4e**,[32] 2-azido-3-methylbenzyl chloride **4f**,[31] 2-azidobenzyl alcohol **16a**,[33] 2-azido-5-methylbenzyl alcohol **16b**,[34] methyl phenyl ketene[35] and diphenyl ketene[36] were prepared by literature procedures.

Preparation of 2-azido-5-bromobenzyl bromide 4b

To a solution of 2-azidobenzyl alcohol **16a** (2.98 g, 20 mmol) in anhydrous tetrahydrofuran (15 ml) *N*-bromosuccinimide (3.56 g, 20 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. After separation of the precipitated succinimide by filtration the solvent was removed under reduced pressure to leave a yellow solid, which was purified by column chromatography [silica gel, using hexanes/ethyl acetate (4 : 1) as eluent] to give **2-azido-5-bromobenzyl alcohol** (3.42 g, 75%).

A solution of bromine (0.64 g, 4 mmol) in anhydrous benzene (5 ml) was added dropwise over 30 min to a stirred solution of triphenylphosphane (1.05 g, 4 mmol) in anhydrous benzene (15 ml) at 0 °C. Then 2-azido-5-bromobenzyl alcohol (0.91 g, 4 mmol) and triethylamine (0.41 g, 4 mmol) were added and the stirring was continued for 3 h. After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel, using hexanes/diethyl ether (9 : 1) as eluent] to give 2-azido-5-bromobenzyl bromide **4b** (0.95 g, 82%) (Found: C, 28.6; H, 1.5; N, 4.5. $C_7H_5Br_2N_3$ requires C, 28.9; H, 1.7; N, 4.8%); ν_{max}(film)/cm^{-1} 2125, 2083, 1482, 1436, 1302, 1217, 1196, 1102, 893, 874 and 811; δ_H (200 MHz; $CDCl_3$; Me_4Si) 4.38 (2 H, s), 7.01 (1 H, d, *J* = 8.5), 7.44 (1 H, dd, *J* = 8.5 and 2.3), 7.49 (1 H, d, *J* = 2.3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 27.1, 117.6 (s), 120.1, 130.8 (s), 132.9, 134.1, 137.8 (s).

Preparation of 3-azido-2-bromomethylnaphthalene 4g

A solution of 3-amino-2-naphthoic acid (0.94 g, 5 mmol) in anhydrous tetrahydrofuran (20 ml) was added dropwise over 30 min to a stirred solution of lithium aluminium hydride (0.47 g, 12.5 mmol) in tetrahydrofuran (20 ml) at 0 °C. The mixture was stirred at room temperature under an atmosphere of nitrogen for 16 h, after which it was cooled and quenched by careful addition of water (20 ml). The mixture was basified with 10% sodium hydroxide (20 ml) and then extracted with diethyl ether (4 × 50 ml). The combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the resulting material was triturated with cold diethyl ether to give **3-amino-2-hydroxymethylnaphthalene** (0.34 g, 39%).

A solution of sodium nitrite (0.43 g, 6.25 mmol) in water (5 ml) was added dropwise over 5 min to a solution of 3-amino-2-hydroxymethylnaphthalene (0.87 g, 5 mmol) in water (10 ml) and concentrated sulfuric acid (2 ml) at 0 °C. The mixture was stirred at that temperature for 30 min. Then a solution of sodium azide (0.57 g, 8.75 mmol) in water (5 ml) was added dropwise over 10 min. After stirring for 5 h the precipitated **3-azido-2-hydroxymethylnaphthalene** was isolated by filtration, washed with water and air dried (0.85 g, 85%).

A solution of bromine (0.64 g, 4 mmol) in anhydrous benzene (5 ml) was added dropwise over 30 min to a stirred solution of triphenylphosphane (1.05 g, 4 mmol) in anhydrous benzene (15 ml) at 0 °C. Then 3-azido-2-hydroxymethylnaphthalene (0.80 g, 4 mmol) and triethylamine (0.41 g, 4 mmol) were added and the stirring was continued for 3 h. After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel, using hexanes/diethyl ether (9 : 1) as eluent] to give 3-azido-2-bromomethylnaphthalene **4g** (0.71 g, 68%) (Found: C, 50.1; H, 2.9; N, 16.3. $C_{11}H_8BrN_3$ requires C, 50.4; H, 3.1; N, 16.0%); ν_{max}(film)/cm^{-1} 2134, 2113, 1622, 1594, 1501, 1288, 1212, 868, 843 and 756; δ_H (200 MHz; $CDCl_3$; Me_4Si) 4.59 (2 H, s), 7.37–7.53 (3 H, m), 7.67–7.77 (2 H, m), 7.81 (1 H, s); δ_C (50 MHz; $CDCl_3$; Me_4Si) 29.1, 116.0, 126.0, 126.5, 127.6, 127.9, 128.4 (s), 130.8 (s), 130.9, 133.9 (s), 136.7 (s).

Preparation of dithiocarbonic acid *O*-ethyl ester *S*-(2-azidobenzyl) esters 5

A solution of potassium *O*-ethyl xanthate (0.80 g, 5 mmol) in anhydrous acetone (20 ml) was added dropwise to a solution of the corresponding 2-azidobenzyl bromide or 2-azidobenzyl chloride **4** (5 mmol) in the same solvent (15 ml), while stirring at room temperature. After 1 h, the KBr was separated by filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel, using hexanes/diethyl ether (9 : 1) as eluent].

Dithiocarbonic acid *O*-ethyl ester *S*-(2-azidobenzyl) ester (5a). (0.92 g, 73%); yellow oil (Found: C, 47.15; H, 4.2; N, 16.8. $C_{10}H_{11}N_3OS_2$ requires C, 47.4; H, 4.4; N, 16.6%); ν_{max}(film)/cm^{-1} 2121, 1582, 1491, 1451, 1292, 1218, 1150, 1112, 1048 and 749; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.41 (3 H, t, *J* = 7.1), 4.31 (2 H, s), 4.64 (2 H, q, *J* = 7.1), 7.03–7.10 (2 H, m), 7.23–7.40 (2 H, m); δ_C (75 MHz;, $CDCl_3$; Me_4Si) 13.8, 35.7, 70.0, 118.2, 124.7, 127.0 (s), 129.1, 131.1, 138.6 (s), 214.0 (s).

Dithiocarbonic acid *O*-ethyl ester *S*-(2-azido-5-bromobenzyl) ester (5b). (1.58, 95%); yellow oil (Found: C, 36.3; H, 3.0; N, 12.5. $C_{10}H_{10}BrN_3OS_2$ requires C, 36.15; H, 3.1; N, 12.65%); ν_{max}(film)/cm^{-1} 2127, 2079, 1299, 1263, 1225, 1119, 1105, 1051, 1004, 893, 872, 804 and 738; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.43 (3 H, t, *J* = 7.0), 4.25 (2 H, s), 4.65 (2 H, q, *J* = 7.0), 7.00 (1 H, d, *J* = 8.4), 7.41 (1 H, dd, *J* = 8.4 and 2.4), 7.54 (1 H, d, *J* = 2.4); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 35.2, 70.3, 117.5 (s), 119.8, 129.5 (s), 132.0, 133.9, 137.9 (s), 213.4 (s).

Dithiocarbonic acid *O*-ethyl ester *S*-(2-azido-5-chlorobenzyl) ester (5c). (1.16 g, 81%); yellow oil (Found: C, 41.5; H, 3.3; N, 14.4. $C_{10}H_{10}ClN_3OS_2$ requires C, 41.7; H, 3.5; N, 14.6%); ν_{max}(film)/cm^{-1} 2128, 2084, 1590, 1490, 1303, 1219, 1150, 1113, 1049, 897 and 815; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.43 (3 H, t, J = 7.1), 4.25 (2 H, s), 4.65 (2 H, q, J = 7.1), 7.07 (1 H, d, J = 8.6), 7.28 (1 H, dd, J = 8.6 and 2.4), 7.40 (1 H, d, J = 2.4); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 35.2, 70.4, 119.4, 129.0, 129.1 (s), 129.8 (s), 131.0, 137.3 (s), 213.4 (s).

Dithiocarbonic acid *O*-ethyl ester *S*-(2-azido-5-methylbenzyl) ester (5d). (1.18 g, 88%); yellow oil (Found: C, 49.4; H, 4.8; N, 15.45. $C_{11}H_{13}N_3OS_2$ requires C, 49.3; H, 4.9; N, 15.7%); ν_{max}(film)/cm^{-1} 2125, 2083, 1498, 1297, 1214, 1146, 1112, 1049 and 808; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.42 (3 H, t, J = 7.2), 2.29 (3 H, s), 4.28 (2 H, s), 4.65 (2 H, q, J = 7.2), 7.01 (1 H, d, J = 8.0), 7.11 (1 H, dd, J = 8.0 and 2.0), 7.18 (1 H, d, J = 2.0); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 20.8, 35.8, 70.0, 118.2, 126.7 (s), 129.8, 131.8, 134.6 (s), 135.9 (s), 214.1 (s).

Dithiocarbonic acid *O*-ethyl ester *S*-(2-azido-4-nitrobenzyl) ester (5e). (1.06, 71%); yellow oil (Found: C, 40.0; H, 3.5; N, 18.6. $C_{10}H_{10}N_4O_3S_2$ requires C, 40.3; H, 3.4; N, 18.8%); ν_{max}(film)/cm^{-1} 2223, 2122, 1525, 1347, 1290, 1221, 1149, 1112, 1044, 1002, 877, 815, 736 and 654; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.43 (3 H, t, J = 7.1), 4.37 (2 H, s), 4.65 (2 H, q, J = 7.1), 7.64 (1 H, d, J = 8.4), 7.93 (1 H, dd, J = 8.4 and 2.1), 8.00 (1 H, d, J = 2.1); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 35.1, 70.6, 113.2, 119.4, 131.7, 134.7 (s), 140.0 (s), 147.3 (s), 213.0 (s).

Dithiocarbonic acid *O*-ethyl ester *S*-(2-azido-3-methylbenzyl) ester (5f). (0.89 g, 67%); yellow oil (Found: C, 49.2; H, 4.8; N, 15.7. $C_{11}H_{13}N_3OS_2$ requires C, 49.4; H, 4.9; N, 15.7%); ν_{max}(film)/cm^{-1} 2099, 1463, 1434, 1292, 1214, 1149, 1112, 1049, 943, 787 and 759; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.42 (3 H, t, J = 7.1), 2.42 (3 H, s), 4.39 (2 H, s), 4.65 (2 H, q, J = 7.1), 7.00–7.12 (2 H, m), 7.25 (1 H, dd, J = 7.0 and 2.0); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 18.0, 37.0, 70.1, 125.9, 128.8, 129.5 (s), 131.2, 133.0 (s), 137.0 (s), 213.9 (s).

Dithiocarbonic acid *O*-ethyl ester *S*-[(3-azido-2-naphthyl)-methyl] ester (5g). (1.38 g, 91%); yellow oil (Found: C, 55.2; H, 4.1; N, 13.7. $C_{14}H_{13}N_3OS_2$ requires C, 55.4; H, 4.3; N, 13.85%); ν_{max}(film)/cm^{-1} 2107, 1598, 1464, 1377, 1287, 1219, 1113, 1052, 871, 760 and 749; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.41 (3 H, t, J = 7.1), 4.44 (2 H, s), 4.64 (2 H, q, J = 7.1), 7.36–7.50 (3 H, m), 7.66–7.76 (2 H, m), 7.85 (1 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 36.2, 70.1, 115.7, 125.8, 126.4, 126.6 (s), 127.1, 127.7, 130.4, 130.7 (s), 133.4 (s), 136.9 (s), 213.9 (s).

Preparation of dithiocarbonic acid *O*-ethyl ester *S*-(2-triphenylphosphoranylideneamino)benzyl esters 6

To a solution of the corresponding azide **5** (5 mmol) in anhydrous diethyl ether (15 ml) triphenylphosphane (1.31 g, 5 mmol) was added. The reaction mixture was stirred at room temperature in an atmosphere of nitrogen for 6 h. Then, the precipitated compounds **6** were isolated by filtration.

These compounds were used in the following step without further purification. For analytical samples compounds **6** were recrystallized from diethyl ether.

Dithiocarbonic acid *O*-ethyl ester *S*-(2-triphenylphosphoranylideneamino)benzyl ester (6a). (2.05 g, 84%); mp 121–122 °C; colourless prisms (Found: C, 68.8; H, 5.25; N, 2.7. $C_{28}H_{26}NOPS_2$ requires C, 69.0; H, 5.4; N, 2.9%); ν_{max}(nujol)/cm^{-1} 1589, 1436, 1340, 1310, 1209, 1107, 1041, 998, 847, 745, 718 and 694; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.41 (3 H, t, J = 7.1), 4.65 (2 H, q, J = 7.1), 4.69 (2 H, s), 6.40 (1 H, d, J = 7.9), 6.57 (1 H, t, J = 7.2), 6.80 (1 H, td, J = 7.6 and 1.5), 7.27–7.32 (1 H, m), 7.38–7.52 (9 H, m), 7.70–7.80 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 39.2, 69.4, 116.8, 120.7 (d, J = 10.2), 128.1, 128.6 (d, J = 11.9), 130.0, 130.1, 130.2 (d, J = 2.5), 130.7 (d, J = 121.3), 131.7 (d, J = 2.8), 132.6 (d, J = 9.6), 150.1 (d, J = 0.7), 217.0 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) 3.6; *m*/*z* (EI) 487 (M^+, 5%), 366 (100).

Dithiocarbonic acid *O*-ethyl ester *S*-(5-bromo-2-triphenylphosphoranylideneamino)benzyl ester (6b). (2.41 g, 85%); mp 123–125 °C; colourless prisms (Found: C, 59.5; H, 4.3; N, 2.4. $C_{28}H_{25}BrNOPS_2$ requires C, 59.3; H, 4.45; N, 2.5%); ν_{max}(nujol)/cm^{-1} 1576, 1437, 1244, 1211, 1110, 1047, 815, 720 and 693; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.46 (3 H, t, J = 7.2), 4.61 (2 H, s), 4.68 (2 H, q, J = 7.2), 6.25 (1 H, d, J = 8.6), 6.88 (1 H, dd, J = 8.6 and 2.6), 7.41–7.55 (10 H, m), 7.70–7.77 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 38.6, 69.7, 108.4, 121.9 (d, J = 10.4), 128.8 (d, J = 12.2), 130.6 (d, J = 99.7), 130.7, 131.9, 132.6 (d, J = 9.9), 149.3 (s), 216.3 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) 4.4; *m*/*z* (EI) 567 (M^+ + 2, 5%), 565 (M^+, 4), 183 (100).

Dithiocarbonic acid *O*-ethyl ester *S*-(5-chloro-2-triphenylphosphoranylideneamino)benzyl ester (6c). (2.35 g, 90%); mp 139–140 °C; colourless prisms (Found: C, 64.2; H, 4.7; N, 2.6. $C_{28}H_{25}ClNOPS_2$ requires C, 64.4; H, 4.8; N, 2.7%); ν_{max}(nujol)/cm^{-1} 1584, 1437, 1348, 1245, 1211, 1183, 1114, 1050, 876, 816, 721 and 693; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.43 (3 H, t, J = 7.1), 4.60 (2 H, s), 4.66 (2 H, q, J = 7.1), 6.28 (1 H, dd, J = 8.5 and 1.0), 6.73 (1 H, dd, J = 8.5 and 2.7), 7.26–7.29 (1 H, m), 7.37–7.55 (9 H, m), 7.67–7.77 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 38.6, 69.7, 121.1 (s), 121.2 (d, J = 13.4), 127.7, 128.7 (d, J = 12.0), 129.7 (d, J = 2.0), 130.5 (d, J = 99.2), 131.4 (s), 131.9 (d, J = 2.6), 132.5 (d, J = 9.7), 148.7 (s), 216.3 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) 4.9; *m*/*z* (EI) 523 (M^+ + 2, 3%), 521 (M^+, 8), 183 (100).

Dithiocarbonic acid *O*-ethyl ester *S*-(5-methyl-2-triphenylphosphoranylideneamino)benzyl ester (6d). (1.88 g, 75%); mp 104–105 °C; colourless prisms (Found: C, 69.2; H, 5.6; N, 2.7. $C_{29}H_{28}NOPS_2$ requires C, 69.4; H, 5.6; N, 2.8%); ν_{max}(nujol)/cm^{-1} 1609, 1438, 1247, 1197, 1108, 1048, 1026, 999, 857, 814, 717 and 696; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.42 (3 H, t, J = 7.2), 2.16 (3 H, s), 4.66 (2 H, q, J = 7.2), 4.67 (2 H, s), 6.31 (1 H, dd, J = 8.0 and 1.0), 6.61 (1 H, dd, J = 8.0 and 2.0), 7.11 (1 H, t, J = 2.0), 7.37–7.51 (9 H, m), 7.71–7.78 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.0, 20.5, 39.2, 69.4, 120.5 (d, J = 9.9), 125.9 (s), 128.6 (d, J = 12.2), 129.5 (d, J = 23.2), 130.6, 131.3 (d, J = 99.7), 131.6, 132.6 (d, J = 9.9), 147.4 (s), 217.0 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) 3.2; *m*/*z* (EI) 501 (M^+, 7%), 380 (100).

Dithiocarbonic acid *O*-ethyl ester *S*-(4-nitro-2-triphenylphosphoranylideneamino)benzyl ester (6e). (2.10 g, 79%); mp 150–152 °C; colourless prisms (Found: C, 63.0; H, 4.6; N, 5.1. $C_{28}H_{25}N_2O_3PS_2$ requires C, 63.2; H, 4.7; N, 5.3%); ν_{max}(nujol)/cm^{-1} 1607, 1560, 1510, 1341, 1294, 1217, 1109, 1044, 862, 813, 740, 718 and 694; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.42 (3 H, t, J = 7.1), 4.66 (2 H, q, J = 7.1), 4.70 (2 H, s), 7.14 (1 H, s), 7.39–7.55 (11 H, m), 7.72–7.83 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 38.3, 69.9, 111.4, 113.7 (d, J = 11.0), 129.0 (d, J = 12.2), 129.5 (d, J = 99.7), 129.7 (d, J = 2.0), 132.2 (d, J = 2.7), 132.5 (d, J = 9.9), 137.8 (d, J = 3.1), 148.0 (s), 151.1 (s), 215.9 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) 7.5; *m*/*z* (EI) 532 (M^+, 6%), 411 (100).

Dithiocarbonic acid *O*-ethyl ester *S*-(3-methyl-2-triphenylphosphoranylideneamino)benzyl ester (6f). (2.51 g, 79%); mp 136–138 °C; colourless prisms (Found: C, 69.3; H, 5.5; N, 2.7. $C_{29}H_{28}NOPS_2$ requires C, 69.4; H, 5.6; N, 2.8%); ν_{max}(nujol)/cm^{-1} 1593, 1435, 1232, 1207, 1113, 1052, 748, 716 and 700; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.33 (3 H, t, J = 7.2), 1.84 (3 H, s), 4.23 (2 H, s), 4.54 (2 H, q, J = 7.2), 6.63 (1 H, td, J = 7.4 and 1.8), 6.91 (1 H, d, J = 7.4), 7.08 (1 H, d, J = 7.4), 7.35–7.51 (9 H,

m), 7.55–7.62 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 21.3, 39.4, 69.2, 118.9, 127.9 (d, J = 1.5), 128.4 (d, J = 12.2), 129.3 (d, J = 9.3), 130.0 (d, J = 2.4), 131.4 (d, J = 2.2), 132.3 (d, J = 9.6), 132.5 (d, J = 97.4), 133.2 (d, J = 4.8), 147.6 (s), 215.8 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) −2.8; *m*/*z* (EI) 501 (M^+, 4%), 294 (100).

Dithiocarbonic acid *O*-ethyl ester *S*-(3-triphenylphosphoranylideneamino-2-naphthyl)methyl ester (6g). (2.46 g, 91%); mp 67–69 °C; colourless prisms (Found: C, 71.2; H, 5.1; N, 2.5. $C_{32}H_{28}NOPS_2$ requires C, 71.5; H, 5.25; N, 2.7%); ν_{max}(nujol)/cm^{-1} 1595, 1438, 1339, 1281, 1213, 1197, 1114 and 1051; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.43 (3 H, t, J = 7.0), 4.66 (2 H, q, J = 7.0), 4.84 (2 H, s), 6.63 (1 H, s), 7.06–7.21 (3 H, m), 7.39–7.52 (9 H, m), 7.59 (2 H, d, J = 7.8), 7.76–7.83 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.0, 39.3, 69.6, 114.5 (d, J = 10.3), 121.7, 125.3, 127.2 (s), 127.3, 128.5, 128.6, 128.7 (d, J = 12.2), 130.7 (d, J = 99.7), 131.8 (d, J = 2.3), 132.7 (d, J = 9.8), 133.0 (s), 134.8 (s), 148.5 (s), 216.6 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) 5.3; *m*/*z* (EI) 537 (M^+, 20%), 183 (100).

Preparation of ketenimines 7

To a solution of the corresponding triphenylphosphazene **6** (2 mmol) in anhydrous dichloromethane (25 ml) a solution of methyl phenyl ketene or diphenyl ketene (2 mmol) in the same solvent (2 ml) was added. After stirring at room temperature for 30 min the solvent was removed under reduced pressure and the resulting material was chromatographed on a silica gel column, using hexanes/diethyl ether (9 : 1) as eluent.

Ketenimine (7a). (0.73 g, 90%); yellow oil (Found: C, 71.1; H, 5.1; N, 3.25. $C_{24}H_{21}NOS_2$ requires C, 71.4; H, 5.4; N, 3.5%); ν_{max}(film)/cm^{-1} 1998, 1596, 1579, 1491, 1454, 1218, 1111, 1048, 760 and 697; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.40 (3 H, t, J = 7.1), 4.58 (2 H, s), 4.63 (2 H, q, J = 7.1), 7.19–7.27 (4 H, m), 7.34–7.36 (9 H, m), 7.48 (1 H, dd, J = 6.9 and 2.1); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 36.4, 70.1, 78.1 (s), 123.0, 126.6, 127.9, 128.0, 128.9, 129.0, 130.7, 131.6 (s), 133.8 (s), 139.4 (s), 190.8 (s), 214.0 (s).

Ketenimine (7b). (0.89 g, 92%); yellow oil (Found: C, 59.5; H, 4.0; N, 2.8. $C_{24}H_{20}BrNOS_2$ requires C, 59.75; H, 4.2; N, 2.9%); ν_{max}(film)/cm^{-1} 1991, 1494, 1475, 1464, 1220, 1172, 1112, 1047, 873, 818, 763 and 694; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.45 (3 H, t, J = 7.2), 4.55 (2 H, s), 4.68 (2 H, q, J = 7.2), 7.23–7.30 (2 H, m), 7.35–7.44 (10 H, m), 7.67 (1 H, d, J = 1.7); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 35.8, 70.3, 78.6 (s), 121.1 (s), 124.4, 126.8, 128.0, 129.0, 132.0, 133.4 (s), 133.7, 134.0 (s), 138.5 (s), 192.0 (s), 213.4 (s).

Ketenimine (7c). (0.81 g, 92%); yellow oil (Found: C, 65.65; H, 4.4; N, 3.0. $C_{24}H_{20}ClNOS_2$ requires C, 65.8; H, 4.6; N, 3.2%); ν_{max}(film)/cm^{-1} 1995, 1599, 1493, 1478, 1219, 1174, 1113, 1047, 899, 822, 761, 695 and 646; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.43 (3 H, t, J = 7.1 Hz), 4.53 (2 H, s), 4.65 (2 H, q, J = 7.1), 7.22–7.41 (12 H, m), 7.49 (1 H, d, J = 1.8); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 35.9, 70.3, 78.6 (s), 124.12, 126.8, 127.9, 129.0, 129.1, 130.7, 133.2 (s), 133.4 (s), 133.8 (s), 137.9 (s), 191.9 (s), 213.4 (s).

Ketenimine (7d). (0.79 g, 94%); yellow oil (Found: C, 71.7; H, 5.4; N, 3.2. $C_{25}H_{23}NOS_2$ requires C, 72.0; H, 5.55; N, 3.35%); ν_{max}(film)/cm^{-1} 1998, 1599, 1492, 1454, 1213, 1150, 1110, 1052, 818, 792, 695 and 646; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.40 (3 H, t, J = 7.2), 2.32 (3 H, s), 4.55 (2 H, s), 4.64 (2 H, q, J = 7.2), 7.07 (1 H, d, J = 8.1), 7.20–7.38 (12 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 21.1, 36.4, 70.0, 78.0 (s), 123.0, 126.5, 127.9, 128.9, 129.8, 131.5, 134.0 (s), 136.7 (s), 138.1 (s), 190.2 (s), 214.1 (s).

Ketenimine (7e). (0.76 g, 85%); yellow oil (Found: C, 64.0; H, 4.3; N, 6.1. $C_{24}H_{20}N_2O_3S_2$ requires C, 64.3; H, 4.5; N, 6.2%); ν_{max}(film)/cm^{-1} 1997, 1527, 1483, 1438, 1348, 1222, 1195, 1119, 1047, 816, 722 and 694; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.40 (3 H, t, J = 7.2), 4.62 (2 H, s), 4.63 (2 H, q, J = 7.2), 7.21–7.30 (2 H, m), 7.34–7.41 (8 H, m), 7.70 (1 H, d, J = 8.4), 8.06 (1 H, dd, J = 8.4 and 2.2), 8.15 (1 H, d, J = 2.2). δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 35.9, 70.6, 77.6 (s), 117.5, 122.1, 127.3, 128.2, 129.2, 131.6, 132.8 (s), 139.2 (s), 141.0 (s), 148.1 (s), 194.2 (s), 213.0 (s).

Ketenimine (7f). (0.70 g, 84%); yellow oil (Found: C, 71.8; H, 5.4; N, 3.2. $C_{25}H_{23}NOS_2$ requires C, 71.9; H, 5.55; N, 3.35%); ν_{max}(film)/cm^{-1} 2012, 1592, 1492, 1463, 1217, 1176, 1115, 1051, 762, 699 and 648; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.36 (3 H, t, J = 7.1), 2.24 (3 H, s), 4.42 (2 H, s), 4.57 (2 H, q, J = 7.1), 7.02–7.10 (2 H, m), 7.17–7.24 (2 H, m), 7.28–7.35 (9 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 19.0, 37.1, 69.9, 73.6 (s), 126.2, 126.5, 128.0, 128.6, 128.9, 129.3 (s), 130.8, 131.9 (s), 134.3 (s), 138.3 (s), 187.1 (s), 213.2 (s).

Ketenimine (7g). (0.72 g, 79%); yellow oil (Found: C, 73.9; H, 5.0; N, 3.0. $C_{28}H_{23}NOS_2$ requires C, 74.1; H, 5.1; N, 3.1%); ν_{max}(film)/cm^{-1} 1997, 1595, 1495, 1461, 1436, 1196, 1119, 1047, 883, 748, 724 and 694; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.45 (3 H, t, J = 7.2), 4.68 (2 H, q, J = 7.2 Hz), 4.75 (2 H, s), 7.26–7.32 (2 H, m), 7.38–7.50 (10 H, m), 7.77–7.83 (3 H, m), 7.99 (1 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.8, 37.0, 70.0, 78.0 (s), 120.8, 126.6, 126.8, 127.5, 127.6, 127.9, 128.9, 129.8 (s), 130.0, 132.4 (s), 133.3 (s), 133.8 (s), 137.4 (s), 190.9 (s), 213.8 (s).

Ketenimine (7h). (0.46 g, 68%); yellow oil (Found: C, 66.7; H, 5.5; N, 4.0. $C_{19}H_{19}NOS_2$ requires C, 66.8; H, 5.6; N, 4.1%); ν_{max}(nujol)/cm^{-1} 2003, 1598, 1582, 1490, 1253, 1219, 1112, 1048, 757 and 692; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.43 (3 H, t, J = 7.2), 2.13 (3 H, 3), 4.60 (2 H, s), 4.66 (2 H, q, J = 7.2), 7.08–7.15 (1 H, m), 7.18–7.27 (5 H, m), 7.29–7.36 (2 H, m), 7.47 (1 H, d, J = 7.2); δ_C (75 MHz; $CDCl_3$; Me_4Si) 12.3, 13.9, 36.5, 67.5 (s), 70.1, 122.8, 124.6, 125.3, 127.4, 128.8, 129.0, 130.9, 131.2 (s), 135.3 (s), 140.4 (s), 194.6 (s).

Preparation of indole 8

A solution of the ketenimine **7c** (0.26 g, 0.6 mmol) in anhydrous cyclohexane (60 ml) was heated at reflux temperature under an atmosphere of nitrogen and lauroyl peroxide was added (0.36 g, 0.9 mmol) portionwise (0.1 mmol every 3 h). After 3 h since the last addition the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography, using hexanes/diethyl ether (7 : 3) as eluent.

After removing the solvent from the column chromatography under reduced pressure the resulting viscous oil was dried at room temperature under high vacuum for 12 h, and used as such for characterization.

Indole (8). (0.12 g, 38%) (Found: C, 76.9; H, 7.2; N, 2.6. $C_{33}H_{38}ClNO_2$ requires C, 76.8; H, 7.4; N, 2.7%); ν_{max}(film)/cm^{-1} 3438, 1706, 1467, 1445, 1312, 1142, 1061, 919, 872, 800, 761 and 702; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (3 H, t, J = 7.0), 1.21–1.26 (16 H, m), 1.52–1.57 (2 H, m), 2.31 (2 H, t, J = 7.4), 6.04 (1 H, d, J = 1.4), 7.09 (1 H, dd, J = 8.6 and 2.0), 7.15 (1 H, d, J = 8.6), 7.28–7.33 (10 H, m), 7.46 (1 H, d, J = 1.4), 8.49 (1 H, br); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.2, 22.8, 24.8, 29.1, 29.3, 29.4, 29.5, 29.7, 32.0, 34.0, 43.5, 79.0 (s), 102.8, 112.1, 120.2, 122.6, 125.6 (s), 127.2, 128.0, 128.3, 129.0 (s), 134.4 (s), 144.3 (s), 145.0 (s), 179.3 (s); *m*/*z* (EI) 518 (M^+ + 2, 9%), 516 (M^+, 12), 314 (100).

Preparation of indoles 9

A solution of the corresponding ketenimine **7** (0.6 mmol) in anhydrous chlorobenzene (60 ml) was heated at reflux temper-

ature under an atmosphere of nitrogen and *t*-butyl peroxide was added (0.10 g, 0.72 mmol) portionwise (0.12 mmol every 4 h). After 4 h since the last addition the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography, using hexanes/diethyl ether (9 : 1) as eluent.

After removing the solvent from the column chromatography under reduced pressure the resulting solid material was triturated, dried at room temperature under high vacuum for 12 h, and used as such for characterization. Compounds **9** were stored in an atmosphere of nitrogen to avoid air oxidation.

2-Diphenylmethylindole (9a). (0.085 g, 50%) (Found: C, 89.3; H, 5.9; N, 4.7. $C_{21}H_{17}N$ requires C, 89.0; H, 6.0; N, 4.9%); ν_{max}(nujol)/cm^{-1} 3400, 1601, 1585, 1290, 1078, 1031, 749 and 700; δ_H (300 MHz; $CDCl_3$; Me_4Si) 5.54 (1 H, s), 6.06 (1 H, d, J = 1.0), 7.00–7.34 (13 H, m), 7.48 (1 H, d, J = 6.8), 7.71 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 51.1, 102.9, 110.7, 119.8, 120.3, 121.6, 127.0, 128.4 (s), 128.7, 129.1, 136.3 (s), 140.9 (s), 142.1 (s); *m*/*z* (EI) 283 (M^+, 100%).

5-Bromo-2-diphenylmethylindole (9b). (0.052 g, 24%) (Found: C, 69.5; H, 4.2; N, 3.7. $C_{21}H_{16}BrN$ requires C, 69.6; H, 4.45; N, 3.9%); ν_{max}(nujol)/cm^{-1} 3300, 1615, 1600, 1279, 1050, 742 and 703; δ_H (300 MHz; $CDCl_3$; Me_4Si) 5.55 (1 H, s), 6.03 (1 H, d, J = 2.0), 7.06 (2 H, d, J = 8.6), 7.16–7.36 (10 H, m), 7.60 (1 H, d, J = 2.0), 7.82 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 51.1, 102.4, 112.1, 113.0 (s), 122.8, 124.4, 127.2, 128.8, 129.0, 130.2 (s), 134.9 (s), 141.8 (s), 142.3 (s); *m*/*z* (EI) 363 (M^+ + 2, 99%), 361 (M^+, 87), 203 (100).

5-Chloro-2-diphenylmethylindole (9c). (0.12 g, 60%) (Found: C, 79.1; H, 5.0; N, 4.2. $C_{21}H_{16}ClN$ requires C, 79.4; H, 5.1; N, 4.4%); ν_{max}(nujol)/cm^{-1} 3417, 1600, 1575, 1309, 1218, 1137, 1061, 919, 867, 796, 748 and 701; δ_H (300 MHz; $CDCl_3$; Me_4Si) 5.50 (1 H, s), 6.00 (1 H, d, J = 1.2), 7.03 (2 H, d, J = 1.2), 7.14–7.34 (10 H, m), 7.42 (1 H, s), 7.74 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 51.0, 102.5, 111.6, 119.6, 121.8, 125.3 (s), 127.1, 128.7, 129.0, 129.4 (s), 134.5 (s), 141.8 (s), 142.4 (s); *m*/*z* (EI) 319 (M^+ + 2, 20%), 317 (M^+, 82), 240 (100).

2-Diphenylmethyl-5-methylindole (9d). (0.084 g, 47%) (Found: C, 88.6; H, 6.5; N, 4.8. $C_{22}H_{19}N$ requires C, 88.85; H, 6.4; N, 4.7%); ν_{max}(nujol)/cm^{-1} 3408, 1600, 1589, 1311, 1291, 1219, 1157, 1030, 802, 747 and 701; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.40 (3 H, s), 5.55 (1 H, s), 6.07 (1 H, s), 6.93 (1 H, d, J = 8.2), 7.09 (1 H, d, J = 8.2), 7.18–7.32 (11 H, m), 7.65 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 21.5, 51.2, 102.4, 110.3, 120.0, 123.2, 127.0, 128.7, 129.1, 134.6 (s), 140.9 (s), 142.3 (s); *m*/*z* (EI) 297 (M^+, 100%).

2-Diphenylmethyl-6-nitroindole (9e). (0.13 g, 64%) (Found: C, 76.7; H, 4.9; N, 8.8. $C_{21}H_{16}N_2O_2$ requires C, 76.8; H, 4.9; N, 8.5%); ν_{max}(nujol)/cm^{-1} 3398, 1592, 1537, 1505, 1337, 1072, 880, 827, 781, 749 and 701; δ_H (300 MHz; $CDCl_3$; Me_4Si) 5.62 (1 H, s), 6.20 (1 H, d, J = 0.9), 7.17–7.35 (10 H, m), 7.47 (1 H, d, J = 8.8), 7.93 (1 H, dd, J = 8.8 and 1.8), 8.15 (1 H, d, J = 1.8), 8.46 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 51.2, 103.7, 107.7, 115.5, 119.9, 127.4, 128.9, 129.0, 133.4 (s), 134.7 (s), 141.2 (s), 142.9 (s), 147.6 (s); *m*/*z* (EI) 328 (M^+, 100%).

2-Diphenylmethyl-7-methylindole (9f). (0.11 g, 60%) (Found: C, 88.6; H, 6.5; N, 4.9. $C_{22}H_{19}N$ requires C, 88.85; H, 6.4; N, 4.7%); ν_{max}(nujol)/cm^{-1} 3438, 1600, 1554, 1298, 1254, 1081, 1032, 796, 748 and 700; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.34 (3 H, s), 5.57 (1 H, s), 6.06 (1 H, d, J = 1.2), 6.92–7.01 (2 H, m), 7.21–7.35 (11 H, m), 7.75 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 16.7, 51.1, 103.6, 118.0, 119.8 (s), 120.0, 122.3, 127.0, 127.9 (s), 128.6, 129.1, 135.9 (s), 140.5 (s), 142.2 (s);. *m*/*z* (EI) 297 (M^+, 100%).

2-Diphenylmethylbenzo[*f*]indole (9g). (0.11 g, 52%) (Found: C, 90.2; H, 5.6; N, 4.2. $C_{25}H_{19}N$ requires C, 90.1; H, 5.7; N, 4.2%); ν_{max}(nujol)/cm^{-1} 3411, 1600, 1584, 1279, 1268, 861, 744 and 698; δ_H (300 MHz; $CDCl_3$; Me_4Si) 5.59 (1 H, s), 6.19 (1 H, d, J = 0.9), 7.21–7.36 (12 H, m), 7.57 (1 H, s), 7.69 (1 H, br s), 7.80 (1 H, dd, J = 7.0 and 2.2), 7.88 (1 H, dd, J = 7.0 and 2.2), 7.96 (1 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 51.4, 102.3, 105.8, 117.5, 122.6, 123.6, 127.2, 127.3, 128.1, 128.7, 129.1, 130.3 (s), 131.0 (s), 137.3 (s), 141.8 (s), 145.2 (s); *m*/*z* (EI) 333 (M^+, 100%).

2-(1-Phenylethyl)indole (9h). (0.058 g, 44%) (Found: C, 86.7; H, 6.9; N, 6.4. $C_{16}H_{15}N$ requires C, 86.8; H, 6.8; N, 6.3%); ν_{max}(nujol)/cm^{-1} 3409, 1618, 1601, 1299, 1153, 1031, 792, 750 and 704; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.71 (3 H, d, J = 7.2), 4.29 (1 H, q, J = 7.2), 6.42 (1 H, s), 7.03–7.13 (2 H, m), 7.19–7.41 (6 H, m), 7.57 (1 H, dd, J = 6.6 and 2.4), 7.67 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 21.3, 39.2, 99.6, 110.5, 119.7, 120.2, 121.4, 126.9, 127.7, 128.5 (s), 128.8, 136.2 (s), 143.1 (s), 144.6 (s); *m*/*z* (EI) 221 (M^+, 69%), 220 (100).

Preparation of indoles 10

A solution of the corresponding ketenimine xanthate **7** (0.6 mmol) in a mixture of methanol and 1,2-dichloroethane (1 : 3; v/v) (60 ml) was heated at reflux temperature under an atmosphere of nitrogen and lauroyl peroxide was added (0.10 g, 0.72 mmol) portionwise (0.12 mmol every 4 h). After 4 h since the last addition the solvent was removed under reduced pressure and the crude residue was purified by chromatography [silica gel, using hexanes/diethyl ether (9 : 1)].

5-Chloro-2-(α-methoxy-α,α-diphenyl)methylindole (10c). (0.090 g, 43%); mp 120–122 °C (from *n*-hexane); colourless prisms (Found: C, 76.3; H, 5.4; N, 4.1. $C_{22}H_{18}ClNO$ requires C, 76.0; H, 5.2; N, 4.0%); ν_{max}(nujol)/cm^{-1} 3430, 1450, 1307, 1255, 1140, 1065, 1050, 804 and 711; δ_H (300 MHz; $CDCl_3$; Me_4Si) 3.13 (3 H, s), 6.48 (1 H, s), 7.07–7.36 (8 H, m), 7.51–7.54 (5 H, m), 8.17 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 52.4, 83.8 (s), 104.5, 112.0, 120.1, 122.6, 125.5 (s), 127.6, 127.8, 128.2, 128.9 (s), 134.2 (s), 141.2 (s), 142.7 (s); *m*/*z* (EI) 349 (M^+ + 2, 12%), 347 (M^+, 35), 315 (100).

2-(α-Methoxy-α,α-diphenyl)methyl-5-methylindole (10d). (0.067 g, 34%); mp 89–91 °C (from *n*-hexane); colourless prisms (Found: C, 84.7; H, 6.2; N, 4.0. $C_{23}H_{21}NO$ requires C, 84.4; H, 6.5; N, 4.3%); ν_{max}(nujol)/cm^{-1} 3454, 1663, 1603, 1450, 1313, 1295, 1224, 1153, 1075, 909, 795 and 737; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.43 (3 H, s), 3.14 (3 H, s), 6.48 (1 H, d, J = 1.5), 6.99 (1 H, dd, J = 8.3 and 1.3), 7.15–7.36 (8 H, m), 7.52–7.57 (4 H, m), 7.98 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 21.5, 52.3, 83.9 (s), 104.9, 110.7, 120.4, 124.0, 127.4, 127.7, 128.0 (s), 128.1, 129.1 (s), 134.3 (s), 139.4 (s), 143.3 (s); *m*/*z* (EI) 327 (M^+, 38%), 298 (100).

Preparation of indole 15

Indole **15** was obtained by reaction of ketenimine **7d** with *t*-butyl peroxide under similar reaction conditions to that of the preparation of indoles **9** but using *ortho*-xylene as solvent.

Indole 15. (0.13 g, 52%) (Found: C, 89.6; H, 6.5; N, 3.4. $C_{30}H_{27}N$ requires C, 89.7; H, 6.8; N, 3.5%); ν_{max}(film)/cm^{-1} 3454, 1600, 1446, 1409, 1313, 1290, 1265, 1037, 872, 797, 741 and 704; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.56 (3 H, s), 2.41 (3 H, s), 3.94 (2 H, s), 6.24 (1 H, d, J = 2.2), 6.82–7.32 (18 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 19.3, 21.5, 41.6, 55.1 (s), 110.3, 120.1, 123.2, 125.5, 126.6, 126.7, 127.9, 128.8 (s), 129.5, 130.0, 130.2, 134.4 (s), 136.5 (s), 139.1 (s), 143.8 (s), 144.8 (s); *m*/*z* (EI) 401 (M^+, 12%), 296 (100).

Preparation of *N*-phenylthioxocarbamate 17

To a solution of 2-azidobenzyl alcohol **16a** (0.74 g, 5 mmol) and phenyl isothiocyanate (0.67 g, 5 mmol) in anhydrous tetrahydrofuran (20 ml) was added sodium hydride (60% in oil; 0.21 g, 5.25 mmol). The reaction mixture was stirred at room temperature in an atmosphere of nitrogen for 16 h, after which the tetrahydrofuran was removed under reduced pressure. The resulting material was partitioned between dichloromethane (25 ml) and water (25 ml). The organic layer was separated and dried over anhydrous magnesium sulfate. After evaporation of the solvent the residue was chromatographed [silica gel, using hexanes/diethyl ether (7 : 3) as eluent] to give **17** (0.88 g, 62%); mp 94–96 °C (from diethyl ether); colourless prisms (Found: C, 59.4; H, 4.3; N, 20.0. $C_{14}H_{12}N_4OS$ requires C, 59.1; H, 4.25; N, 19.7%); ν_{max}(nujol)/cm^{-1} 3231, 2131, 2086, 1556, 1526, 1294, 1223, 1206, 1180, 1059, 1036, 912, 750 and 695; δ_H (300 MHz; $CDCl_3$; Me_4Si) 5.58 (2 H, s), 7.09–7.43 (9 H, m), 8.54 (1 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 69.5 (br), 118.3, 121.8 (br), 124.8 (s), 125.6 (br), 129.0, 130.0, 130.6, 136.9 (s, br), 138.7 (s), 188.1 (s); *m*/*z* (EI) 284 (M$^+$, 7%), 256 (38), 136 (100).

Preparation of *S*-methyl xanthate 18

To a solution of 2-azido-5-methylbenzyl alcohol **16b** (0.82 g, 5 mmol) and carbon disulfide (38 g, 0.5 mol) in anhydrous tetrahydrofuran (60 ml) was added sodium hydride (60% in oil, 3 g, 75 mmol). The reaction mixture was stirred in an atmosphere of nitrogen at room temperature for 2 h and then at 50 °C for 1 h, after which methyl iodide (10.64 g, 75 mmol) was added. The reaction mixture was stirred at 50 °C for 6 h. After cooling the tetrahydrofuran was removed under reduced pressure, and the resulting material was partitioned between dichloromethane (25 ml) and water (25 ml). The organic layer was separated and dried over anhydrous magnesium sulfate. After evaporation of the solvent the residue was chromatographed [silica gel, using hexanes/ethyl acetate (9 : 1) as eluent] to give **18** (1.2 g, 95%); mp 48–49 °C (from *n*-hexane); colourless prisms (Found: C, 47.2; H, 4.3; N, 16.4. $C_{10}H_{11}N_3OS_2$ requires C, 47.4; H, 4.4; N, 16.6%); ν_{max}(nujol)/cm^{-1} 2128, 2103, 1587, 1318, 1245, 1205, 1067, 972, 814, 772 and 726; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.33 (3 H, s), 2.57 (3 H, s), 5.54 (2 H, s), 7.05–7.09 (1 H, s), 7.19 (2 H, br s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 19.2, 20.8, 70.9, 118.2, 125.6 (s), 130.8, 131.4, 134.7 (s), 136.1 (s), 215.6 (s).

Preparation of thionocarbonate 19

A solution of phenyl chlorothionoformate (0.86 g, 5 mmol) in acetonitrile (5 ml) was added dropwise to a stirred solution of 2-azido-5-methylbenzyl alcohol **16b** (0.82 g, 5 mmol) and 4-dimethylaminopyridine (0.92 g, 7.5 mmol) in acetonitrile (30 ml). The reaction mixture was stirred in an atmosphere of nitrogen for 1 h, after which the acetonitrile was removed under reduced pressure. The resulting material was partitioned between dichloromethane (25 ml) and water (25 ml). The organic layer was separated and dried over anhydrous magnesium sulfate. After evaporation of the solvent the residue was chromatographed [silica gel, using hexanes/ethyl acetate (9 : 1) as eluent] to give **19** (0.96 g, 64%); mp 82–84 °C (from diethyl ether/*n*-hexane); colourless prisms (Found: C, 60.0; H, 4.3; N, 14.3. $C_{15}H_{13}N_3O_2S$ requires C, 60.2; H, 4.4; N, 14.0%); ν_{max}(nujol)/cm^{-1} 2127, 2095, 1297, 1284, 1217, 1203, 1012, 849, 772, 713 and 686; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.33 (3 H, s), 5.47 (2 H, s), 7.11–7.45 (8 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 20.8, 71.3, 118.2, 121.9, 124.9 (s), 126.6, 129.5, 131.0, 131.4, 134.7 (s), 136.1 (s), 153.5 (s), 194.9 (s).

Preparation of triphenylphosphazenes 20–22

To a solution of the corresponding azide **17**–**19** (5 mmol) in anhydrous diethyl ether (15 ml) triphenylphosphane (1.31 g, 5 mmol) was added. The reaction mixture was stirred at room temperature under an atmosphere of nitrogen for 6 h. Then, the precipitated compounds **20**–**22** were isolated by filtration.

Triphenylphosphazene 20. (2.25 g, 87%); mp 81–82 °C (from diethyl ether); colourless prisms (Found: C, 74.4; H, 5.0; N, 5.3. $C_{32}H_{27}N_2OPS$ requires C, 74.1; H, 5.25; N, 5.4%); ν_{max}(nujol)/cm^{-1} 3057, 1589, 1482, 1434, 1210, 1181, 1110, 1042, 1019, 999, 847, 823, 746, 718 and 696; δ_H (300 MHz; $CDCl_3$; Me_4Si) 4.52 (2 H, s), 6.43 (1 H, d, *J* = 7.4), 6.61 (1 H, td, *J* = 7.4 and 0.8), 6.79 (1 H, td, *J* = 7.4 and 1.8), 7.02 (1 H, td, *J* = 7.4 and 1.2), 7.18–7.23 (2 H, m), 7.29–7.52 (13 H, m), 7.52–7.77 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 33.0, 117.5, 120.1, 120.9 (d, *J* = 9.9), 124.0, 127.8, 128.7 (d, *J* = 11.6), 128.9, 130.0, 130.5 (s), 131.7 (d, *J* = 2.3), 132.6 (d, *J* = 9.8), 138.2 (s), 149.6 (s), 167.6 (s); δ_P (121.4 MHz, $CDCl_3$, H_3PO_4) 4.03; *m*/*z* (EI) 400 (3%), 278 (19), 277 (100), 240 (25).

Triphenylphosphazene 21. (2.22 g, 91%); mp 168–170 °C (from diethyl ether); colourless prisms (Found: C, 68.7; H, 5.1; N, 2.7. $C_{28}H_{26}NOPS_2$ requires C, 69.0; H, 5.4; N, 2.9%); ν_{max}(nujol)/cm^{-1} 1639, 1609, 1435, 1128, 1112, 1038, 998, 892, 878, 813, 719 and 695; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.15 (3 H, s), 2.39 (3 H, s), 4.52 (2 H, s), 6.30 (1 H, d, *J* = 8.0), 6.60 (1 H, dd, *J* = 8.0 and 2.2), 7.09 (1 H, s), 7.39–7.51 (9 H, m), 7.71–7.77 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.1, 20.5, 33.6, 120.4 (d, *J* = 9.9 Hz), 126.1 (s), 128.6 (d, *J* = 11.6), 128.7, 130.4 (s), 130.7, 131.3 (d, *J* = 103.2), 131.6 (d, *J* = 2.9), 132.6 (d, *J* = 9.9), 147.3 (s), 191.4 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) 2.41; *m*/*z* (EI) 487 (M$^+$, 13%), 183 (100).

Triphenylphosphazene 22. (2.37 g, 89%); mp 163–164 °C (from diethyl ether); colourless prisms (Found C, 74.0; H, 5.5; N, 2.3. $C_{33}H_{28}NO_2PS$ requires C, 74.3; H, 5.3; N, 2.6%); ν_{max}(nujol)/cm^{-1} 1717, 1609, 1438, 1331, 1188, 1114, 1087, 1022, 999, 746, 720 and 691; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.16 (3 H, s), 4.46 (2 H, s), 6.33 (1 H, d, *J* = 8.0), 6.63 (1 H, dd, *J* = 8.0 and 2.0), 7.10–7.22 (4 H, m), 7.31–7.36 (2 H, m), 7.40–7.53 (9 H, m), 7.73–7.80 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 20.5, 34.7, 120.4 (d, *J* = 9.9), 121.6, 125.8, 126.1 (s), 128.6 (d, *J* = 12.2), 129.4, 130.6, 130.8 (s), 131.3 (d, *J* = 102.6), 131.7 (d, *J* = 2.3), 132.6 (d, *J* = 9.9), 147.2 (s), 151.6 (s), 172.1 (s); δ_P (121.4 MHz; $CDCl_3$; H_3PO_4) 2.84; *m*/*z* (EI) 533 (M$^+$, 5%), 194 (100).

Preparation of isothiocyanate 26

To a solution of triphenylphosphazene **6d** (1.25 g, 2.5 mmol) in anhydrous benzene (15 ml) carbon disulfide was added (10 ml). The mixture was stirred at reflux temperature for 12 h. The solvent was removed under reduced pressure and the residue was chromatographed [silica gel, using hexanes/dichloromethane (4 : 1) as eluent] to give **26** (0.69 g, 98%); mp 29–30 °C (from *n*-hexane); colourless prisms (Found: C, 50.7; H, 4.3; N, 4.8. $C_{12}H_{13}NOS_3$ requires C, 50.85; H, 4.6; N, 4.9%); ν_{max}(nujol)/cm^{-1} 2102, 1251, 1218, 1113, 1050, 1011, 947, 914, 875, 824 and 744; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.44 (3 H, t, *J* = 7.1), 2.35 (3 H, s), 4.37 (2 H, s), 4.67 (2 H, q, *J* = 7.1), 7.06 (1 H, dd, *J* = 8.1 and 1.5), 7.15 (1 H, d, *J* = 8.1), 7.23 (1 H, d, *J* = 1.5); δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.9, 21.3, 36.6, 70.4, 126.9, 128.0 (s), 129.7, 131.3, 131.7 (s), 136.6 (s), 137.7 (s), 213.1 (s); *m*/*z* (EI) 283 (M+, 51%), 162 (100).

Reaction of isothiocyanate 26 with lauroyl peroxide

A solution of isothiocyanate **26** (0.17 g, 0.6 mmol) in anhydrous cyclohexane (60 ml) was heated in an atmosphere of nitrogen to reflux and lauroyl peroxide added (0.24 g, 0.6 mmol) portionwise (0.1 mmol every 3 h). After 3 h since the last addition the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography [using hexanes/dichloromethane (4 : 1) as eluent] to give **28** (0.095 g, 98%); mp 134–135 °C (from *n*-hexane); colourless prisms

(Found: C, 66.4; H, 4.9; N, 8.3. $C_{18}H_{16}N_2S_2$ requires C, 66.6; H, 5.0; N, 8.6%); ν_{max}(nujol)/cm^{-1} 2144, 948, 902 and 816; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.33 (6 H, s), 2.92 (4 H, s), 7.00 (2 H, dd, J = 8.1 and 1.5), 7.07 (2 H, d, J = 1.5), 7.09 (2 H, d, J = 8.1); δ_C (75 MHz; $CDCl_3$; Me_4Si) 21.3, 33.3, 126.3, 127.2 (s), 128.3, 131.2, 134.5 (s), 137.1 (s), 137.9 (s); *m/z* (EI) 324 (M^+, 71%), 162 (100).

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