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# The Reaction of (2-Alkylidenaminophenyl)sulfides with Di-iso-propyl Peroxydicarbonate: Radical versus non-Radical Pathway

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*Key Words:* imidoyl radicals; homolytic intramolecular substitution at sulfur; peroxydicarbonate; imines; non-radical attack at peroxides.

***Abstract:*** *The reaction of 2-methylthio- or 2-phenylthioarylimines with di-iso-propyl peroxydicarbonate (DPDC) is described. The phenylthio-derivatives undergo cyclization to benzothiazoles via a free-radical mechanism, whereas the methylthio-analogs afford arylthiomethyl iso-propyl carbonates, together with benzothiazoles as well; this last result could be accounted for with the intervention of a non-radical mechanism operating side by side with the radical one.*

## INTRODUCTION

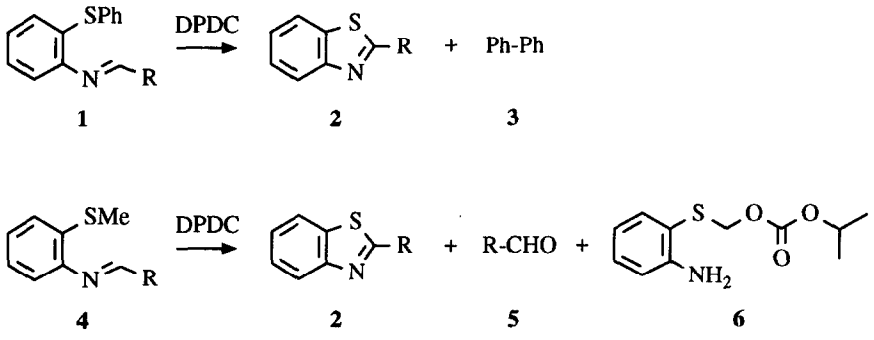
Recently, imidoyl radicals have been studied intensively, and their usefulness in organic synthesis has been proved. These intermediates were generated by hydrogen abstraction from aromatic imines,[1] by reaction of stannyl radicals with selenoimidates[2] or isothiocyanates,[3] or, very recently, by addition of carbon radicals to isonitriles;[4] furthermore, their reactivity with respect to aromatic rings,[1a] double[1d,2,3] or triple C-C bonds,[1b-d,4] and the N-N double bond of diethyl azodicarboxylate[1e] was investigated. As far as the reactivity of imidoyl radicals towards sulfur atoms is concerned, until now there is only one example[1a] which suggests that a substitution reaction might be possible *via* an $S_Hi$ mechanism.

The homolytic intramolecular substitution at the sulfur atom of sulfides is not very common, but it does occur when the leaving group is a stable radical[5] or cyclic products are formed; in this last case, aryl[6]- or vinyl-type radicals[7] are known to cyclize readily even with expulsion of a methyl radical.

We now report the reaction of two series of aromatic imidoyl radicals bearing a methylthio- or a phenylthio-group in a position suitable for 5-membered cyclization to benzothiazoles.

## RESULTS AND DISCUSSION

Imidoyl radicals were generated by iminic hydrogen abstraction with di-*iso*-propyl peroxydicarbonate (DPDC), and the corresponding imines were prepared by reaction of aldehydes with 2-methylthio- or 2-phenylthioaniline; the imines **1** and **4** (5 mmol) were allowed to react with DPDC (10 mmol) in benzene (50 mL) solution for 4-5 h, and the final mixtures were chromatographed to give the products reported in Scheme 1 and Table 1.



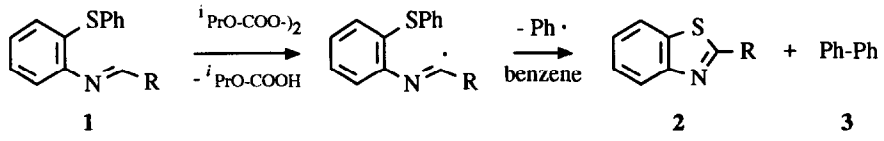

Scheme n. 1.

Table 1. Products Yields for the Reactions of Imines **1** and **4** with DPDC[a].

| Imine | R | **2** Yield, % | **3** Yield, % | **5** Yield, % | **6** Yield, % |
|---|---|---|---|---|---|
| **1a** | Ph | 64 | 35 | - | - |
| **1b** | 4-Cl-$C_6H_4$ | 64 | 30 | - | - |
| **1c** | 4-MeO-$C_6H_4$ | 55 | 32 | - | - |
| **1d** | 3-$O_2N$-$C_6H_4$ | 50 | 20 | - | - |
| **1e** | 2-thienyl | 30 | 15 | - | - |
| **1f** | 2-naphthyl | 50 | 20 | - | - |
| **4a** | Ph | 17 | - | 35 | 53 |
| **4b** | 4-Cl-$C_6H_4$ | 36 | - | 48 | 54 |
| **4c** | 4-MeO-$C_6H_4$ | 28 | - | 48 | 39 |
| **4d** | 3-$O_2N$-$C_6H_4$ | 38 | - | 40 | 35 |
| **4e** | 2-thienyl | 13 | - | 40 | 45 |
| **4g** | Ph-CH=CH | 24 | - | 36 | 30 |

[a] All yields are for isolated pure products and are based on the starting imine.

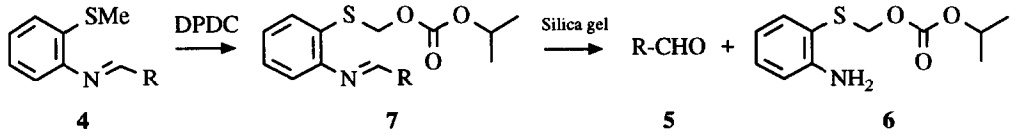
The reactions of the imines **1** afforded benzothiazoles **2** in good to fair yields and biphenyl **3** through the radical pathway shown in Scheme 2.




Scheme n. 2.

The radical nature of the above mechanism is supported by the formation of biphenyl: when the reaction was performed in chlorobenzene or anisole solutions, the ratios of the isomeric *ortho*, *meta*, and *para* chloro- and methoxybiphenyls obtained were identical to those reported for the homolytic phenylation of chlorobenzene and anisole.[8]

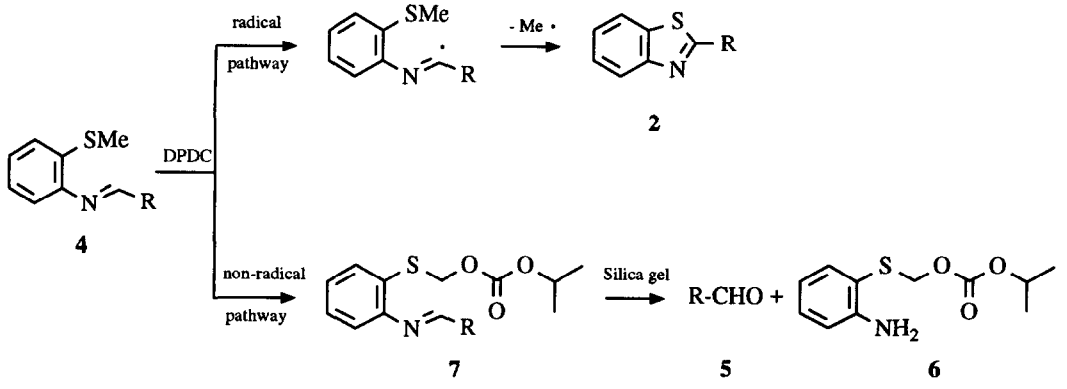
With the imines **4**, the benzothiazoles **2** were not the main reaction products, and substantial amounts of aldehydes **5** and carbonates **6** were formed. These compounds derive from the imino-carbonates **7**, which arise from the reaction of methylthio-group with DPDC, and hydrolyze during chromatographic work-up (Scheme 3).



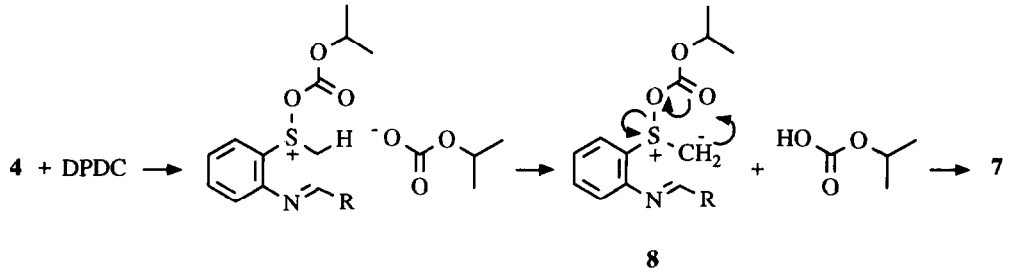

Scheme n. 3.

This hypothesis accounts for the recovery of high amounts of aldehydes: if they were formed during the reaction, because of the oxidative conditions, they would reasonably give rise to the corresponding carboxylic acids. In addition, a careful MS analysis of the reaction mixture, before chromatographic work-up, showed high amounts of imino-carbonate **7** and only trace amounts of **5** and **6**; when the same analysis was carried out on the mixture kept overnight on silica gel, no imino-carbonate **7** was detected, and the derivatives **5** and **6** were the only compounds we observed. Finally, with the imine **4d**, the greater stability due to the nitro-substituent together with a fast column chromatography of the reaction mixture, allowed us to obtain **7d** in high yield.

As far as the mechanism of the reaction is concerned, we could suggest the two pathways shown in Scheme 4. Reactions of methyl sulfides with peroxydicarbonates were not previously described, but a few examples are reported in the literature dealing with the decomposition of di-benzoylperoxide in the presence of thioanisoles;[9] these reactions are supposed to be ionic processes in which the sulfur atom of the sulfide behaves as a nucleophile towards the oxygen-oxygen bond of the peroxide. A mechanism similar to that proposed by Prior and Bickley[9b] could operate (Scheme 5), in which the product **7** might arise from the rearrangement of the ylide **8**.




Scheme n. 4.

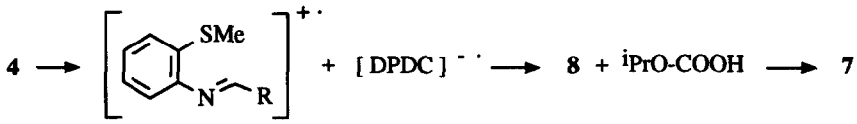



Scheme n. 5.

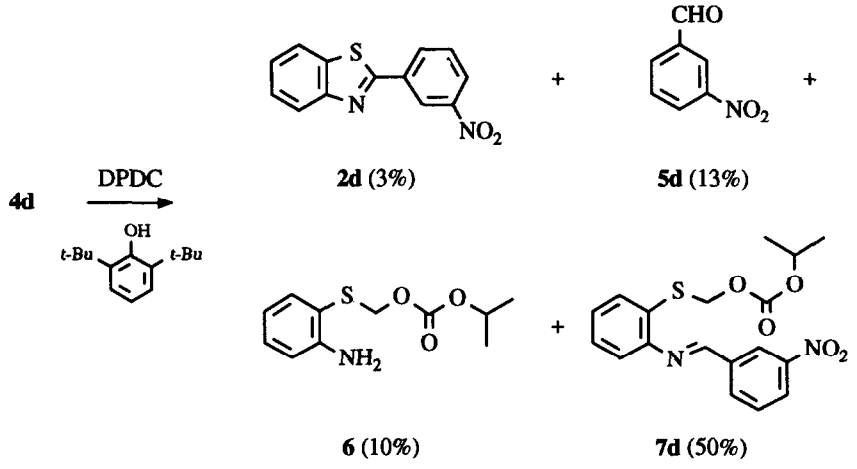
In the case of the imines **1**, this reaction could be hindered by the lower nucleophilicity of aryl sulfides relative to their methyl analogs[10] and by the absence of α-hydrogens, necessary to allow the formation of the corresponding ylide.

As it is known that carbonyl-containing peroxides are good electron-acceptors,[11] we cannot exclude a mechanism involving initial electron-transfer between imine and peroxide, followed by collapse of the ion-pair (Scheme 6).

On the other hand, DPDC can also decompose homolytically, giving rise to intermediates which abstract the iminic hydrogen and originate the imidoyl radicals, with subsequent cyclization to benzothiazoles **2** (radical pathway). In order to demonstrate that two different mechanisms can operate at the same time, we performed the reaction of the imine **4d** with DPDC in the presence of 2,6-di-*tert*-butylphenol as a radical scavenger (Scheme 7).




Scheme n. 6.




Scheme n. 7.

The radicals arising from thermal decomposition of DPDC were scavenged and the radical cyclization product **2d** practically disappeared from the final mixture; the scavenger did not affect the concomitant non-radical pathway and, after fast chromatographic work-up, compound **7d** was obtained in good yields, together with little amounts of hydrolysis products **5d** and **6**. This result led us to exclude also the intervention, in the formation of compounds **7** and **6**, of an arylthiomethyl radical, arising from direct hydrogen abstraction from the methylthio group of **4**.[12] This process might be slow with respect to the other possibilities; in fact, thioanisole reacts with DPDC to afford only phenylthiomethyl *iso*-propyl carbonate, and no product was found deriving from phenylthiomethyl radicals.

The total yields of products arising from the non-radical mechanism were ca. 60% in the presence of a radical scavenger, and ca. 40% in the absence of any inhibitor; the better yields we got in the first case could be obviously explained in terms of disappearance of the homolytic mechanism; on the other hand, for the reaction without scavenger, the intervention of an induced homolytic decomposition of the peroxide, which might increase the rate of the free-radical process, cannot be excluded.[13]

In the light of these results we are not able to distinguish between the two possible mechanisms reported in Schemes 5 and 6, accounting for the formation of the iminocarbonate **7**; in fact, a radical scavenger would not necessarily be able to affect an electron-transfer process, as we observed in a previous paper.[14]

## EXPERIMENTAL SECTION

*General procedures.*

Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. $^1$H-NMR spectra were recorded in deuteriochloroform on Varian EM360L (60 MHz) or Varian Gemini 200 (200 MHz) instruments, using tetramethylsilane as an internal standard. Mass spectra and high resolution mass spectra (HRMS) were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. IR spectra were recorded in trichloromethane on a Perkin-Elmer 257 spectro- photometer. Gas-chromatography was carried out on a Varian 3700 instrument equipped with a Supelco 3% SE30 column and a FID detector. Column chromatography was performed on silica gel (ICN Silica, 63-200, 60A) or neutral aluminum oxide (Merck Aluminiumoxid 90 Aktiv, 70-230, Brockmann III), using light petroleum (40-70 °C) and a light petroleum/diethyl ether gradient (from 0 up to 100% diethyl ether) as eluant. Previously reported reaction products were identified by spectral comparison and mixed mp determination with authentic specimens.

*Starting materials.*

2-Phenylthiobenzenamine,[15] imine **4a**,[16] and di-*iso*-propyl peroxydicarbonate (DPDC)[17] were prepared according to the literature; DPDC was stored at 5 °C as a benzene solution and the peroxide content was determined by iodometric titration.[18]

*Synthesis of imines **1** and **4**.*

*General procedure.* A benzene (100 mL) solution of aldehyde (15 mmol) and amine (15 mmol) was refluxed for 4-5 h, with azeotropic removal of water, in the presence of catalytic amounts of *p*-toluenesulfonic acid (0.1 g). The solvent was evaporated under reduced pressure and the residue distilled or recrystallized from a suitable solvent. According to this general procedure, the following imines were prepared.

*N-Phenylmethylene-2-phenylthiobenzenamine (**1a**).* Benzaldehyde (1.59 g) and 2-phenylthiobenzenamine (3.02 g) gave **1a** (2.90 g, 67%), mp = 95-97 °C (from light petroleum); 60-MHz $^1$H-NMR δ 6.87-7.57 (12 H, m, Ar-*H*), 7.70-8.00 (2 H, m, Ar-*H*), 8.27 (1 H, s, -N=C*H*-); MS *m/e* 289 ($M^+$, 37), 288 (15), 212 (100), 184 (17), 109 (20), 77 (14), 51 (14); HRMS calcd for $C_{19}H_{15}NS$ 289.09252, found 289.09221. Anal. calcd for $C_{19}H_{15}NS$: C, 78.86; H, 5.22; N, 4.84; S, 11.08. Found: C, 78.64; H, 5.20; N, 4.85; S, 11.22.

*N-(4-Chlorophenylmethylene)-2-phenylthiobenzenamine (**1b**).* 4-Chlorobenzaldehyde (2.11 g) and 2-phenylthiobenzenamine (3.02 g) yielded[19] **1b** (2.50 g, 52%), mp = 54-56 °C (from 2-propanol); 60-MHz $^1$H-NMR δ 6.93-7.60 (11 H, m, Ar-*H*), 7.70-7.97 (2 H, part of AA'BB', *J* = 8.00 Hz, Ar-*H*), 8.30 (1 H, s, -N=C*H*-); MS *m/e* 325 ($M^+$+2, 17), 324 ($M^+$+1, 16), 323 ($M^+$, 45), 322 (20), 248 (4), 246 (10), 212 (100), 184 (13), 109 (15); HRMS calcd for $C_{19}H_{14}ClNS$ 323.05355, found 323.05398. Anal. calcd for $C_{19}H_{14}ClNS$: C, 70.46; H, 4.36; Cl, 10.95; N, 4.33; S, 9.90. Found: C, 70.65; H, 4.34; Cl, 10.89; N, 4.35; S, 9.85.

*N-(4-Methoxyphenylmethylene)-2-phenylthiobenzenamine (**1c**).* 4-Methoxybenzaldehyde (2.04 g) and 2-phenylthiobenzenamine (3.02 g) afforded **1c** (3.11 g, 65%), mp = 102-104 °C (from ethanol); 60-MHz $^1$H-NMR δ 3.73 (3 H, s, -OC$H_3$), 6.50-7.90 (13 H, m, Ar-*H*), 8.17 (1 H, s, -N=C*H*-); MS *m/e* 319 ($M^+$, 90), 318 (54), 242 (12), 227 (6), 212 (100), 135 (62); HRMS calcd for $C_{20}H_{17}NOS$ 319.10309, found 319.10336. Anal. calcd for $C_{20}H_{17}NOS$: C, 75.20; H, 5.36; N, 4.38; S, 10.04. Found: C, 74.88; H, 5.33; N, 4.35; S, 10.10.

*N-(3-Nitrophenylmethylene)-2-phenylthiobenzenamine (**1d**).* 3-Nitrobenzaldehyde (2.27 g) and 2-phenylthiobenzenamine (3.02 g) gave **1d** (3.51 g, 70%), mp = 102-105 °C (from cold diethyl ether); 60- MHz

$^1$H-NMR δ 6.80-7.67 (10 H, m, Ar-*H*), 8.00-8.65 (4 H, m, Ar-*H* + -N=C*H*-); MS *m/e* 334 ($M^+$, 46), 333 (9), 304 (2), 287 (4), 257 (6), 212 (100), 150 (36); HRMS calcd for $C_{19}H_{14}N_2O_2S$ 334.07760, found 334.07820. Anal. calcd for $C_{19}H_{14}N_2O_2S$: C, 68.25; H, 4.22; N, 8.38; S, 9.59. Found: C, 67.91; H, 4.19; N, 8.33; S, 9.66.

*N-(2-Thienylmethylene)-2-phenylthiobenzenamine (**1e**).* 2-Thiophenecarboxaldehyde (1.68 g) and 2-phenylthiobenzenamine (3.02 g) yielded[20] **1e** (2.88 g, 65%), bp (0.02 mmHg) = 164-167 °C; 60-MHz $^1$H-NMR δ 6.83-7.50 (12 H, m, Ar-*H*), 8.33 (1 H, s, -N=C*H*-); MS *m/e* 295 ($M^+$, 100), 294 (89), 262 (4), 218 (22), 212 (39), 186 (39); HRMS calcd for $C_{17}H_{13}NS_2$ 295.04894, found 295.04886. Anal. calcd for $C_{17}H_{13}NS_2$: C, 69.11; H, 4.44; N, 4.74; S, 21.71. Found: C, 68.78; H, 4.41; N, 4.72; S, 21.90.

*N-(2-Naphthylmethylene)-2-phenylthiobenzenamine (**1f**).* 2-Naphthalenecarboxaldehyde (2.34 g) and 2-phenylthiobenzenamine (3.02 g) afforded **1f** (3.56 g, 70%), mp = 128-130 °C (from ethanol); 60-MHz $^1$H-NMR δ 6.57-8.33 (17 H, m, Ar-*H* + -N=C*H*-); MS *m/e* 339 ($M^+$, 43), 338 (17), 262 (9), 212 (100); HRMS calcd for $C_{23}H_{17}NS$ 339.10817, found 339.10832. Anal. calcd for $C_{23}H_{17}NS$: C, 81.37; H, 5.05; N, 4.13; S, 9.45. Found: C, 81.65; H, 5.02; N, 4.10; S, 9.55.

*N-(4-Chlorophenylmethylene)-2-methylthiobenzenamine (**4b**).* 4-Chlorobenzaldehyde (2.11 g) and 2-methylthiobenzenamine (2.09 g) gave **4b** (2.82 g, 72%), mp = 90-92 °C (from light petroleum/benzene 70:30 v/v); 60-MHz $^1$H-NMR δ 2.37 (3 H, s, -SC*H*$_3$), 6.85-7.17 (4 H, m, Ar-*H*), 7.22-7.90 (4 H, AA'BB', *J* = 8.4 Hz, 4-Cl-C$_6$*H*$_4$-), 8.27 (1 H, s, -N=C*H*-); MS *m/e* 263 ($M^+$+2, 39), 261 ($M^+$, 100), 248 (17), 246 (45), 230 (17), 228 (50), 216 (6), 214 (15), 193 (22), 150 (20), 138 (14), 136 (23), 109 (33); HRMS calcd for $C_{14}H_{12}ClNS$ 261.03790, found 261.03709. Anal. calcd for $C_{14}H_{12}ClNS$: C, 64.24; H, 4.62; Cl, 13.54; N, 5.35; S, 12.25. Found: C, 64.01; H, 4.59; Cl, 13.68; N, 5.39; S, 12.42.

*N-(4-Methoxyphenylmethylene)-2-methylthiobenzenamine (**4c**).* 4-Methoxybenzaldehyde (2.72 g) and 2-methylthiobenzenamine (2.09 g) yielded **4c** (2.89 g, 75%), mp = 71-73 °C (from light petroleum/benzene 70:30 v/v); 60-MHz $^1$H-NMR δ 2.37 (3 H, s, -SC*H*$_3$), 3.73 (3 H, s, -OC*H*$_3$), 6.72-7.17 (6 H, m, Ar-*H*), 7.68-7.93 (2 H, part of AA'BB', *J* = 8.4 Hz, 4-MeO-C$_6$*H*$_4$-), 8.27 (1 H, s, -N=C*H*-); MS *m/e* 257 ($M^+$, 11), 242 (2), 224 (7), 210 (2), 152 (100), 135 (95); HRMS calcd for $C_{15}H_{15}NOS$ 257.08744, found 257.08749. Anal. calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.44; S, 12.46. Found: C, 69.42; H, 5.83; N, 5.47; S, 12.58.

*N-(3-Nitrophenylmethylene)-2-methylthiobenzenamine (**4d**).* 3-Nitrobenzaldehyde (2.26 g) and 2-methylthiobenzenamine (2.09 g) gave **4d** (2.86 g, 70%), mp = 126-128 °C (from ethanol); 60-MHz $^1$H-NMR δ 2.43 (3 H, s, -SC*H*$_3$), 6.80-7.23 (4 H, m, Ar-*H*), 7.38-7.72 (1 H, dd, *J* = 7.2, 8.4 Hz, Ar-*H*), 8.10-8.35 (2 H, m, Ar-*H*), 8.42 (1 H, s, -N=C*H*-), 8.58-8.72 (1 H, m, Ar-*H*); MS *m/e* 272 ($M^+$, 100), 257 (30), 239 (27), 225 (7), 211 (30), 210 (16), 193 (18), 179 (10), 150 (33); HRMS calcd for $C_{14}H_{12}N_2O_2S$ 272.06195, found 272.06228. Anal. calcd for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29; S, 11.77. Found: C, 61.51; H, 4.42; N, 10.18; S, 11.89.

*N-(2-Thienylmethylene)-2-methylthiobenzenamine (**4e**).* 2-Thiophenecarboxaldehyde (1.68 g) and 2-methylthiobenzenamine (2.09 g) afforded[20] **4e** (2.80 g, 80%), bp (0.01 mmHg) = 138-141 °C, mp = 52-54 °C (from light petroleum); 60-MHz $^1$H-NMR δ 2.38 (3 H, s, -SC*H*$_3$), 6.77-7.20 (5 H, m, Ar-*H*), 7.28-7.50 (2 H, m, Ar-*H*), 8.40 (1 H, s, -N=C*H*-); MS *m/e* 233 ($M^+$, 100), 218 (45), 200 (62), 186 (36), 136 (44), 110 (22), 109 (31); HRMS calcd for $C_{12}H_{11}NS_2$ 233.03329, found 233.03345. Anal. calcd for $C_{12}H_{11}NS_2$: C, 61.77; H, 4.75; N, 6.00; S, 27.48. Found: C, 61.49; H, 4.72; N, 5.96; S, 27.63.

*N-(3-Phenyl-2-propenylidene)-2-methylthiobenzenamine (4g).* 3-Phenyl-2-propenal (1.98 g) and 2-methylthiobenzenamine (2.09 g) yielded **4g** (2.54 g, 67%), mp = 82-84 °C (from ethanol); 60-MHz $^1$H-NMR δ 2.38 (3 H, s, -SC*H*$_3$), 6.70-7.67 (11 H, m, Ar-*H* + -N=C*H*- + Ph-C*H*=CH-), 7.98-8.18 (1 H, dd, *J* = 2.4, 5.8 Hz, -N=CH-C*H*=CH-); MS *m/e* 253 (M$^+$, 100), 252 (79), 238 (56), 236 (37), 220 (31), 206 (24), 204 (27), 176 (7), 130 (24); HRMS calcd for $C_{16}H_{15}NS$ 253.09252, found 253.09189. Anal. calcd for $C_{16}H_{15}NS$: C, 75.84; H, 5.97; N, 5.53; S, 12.66. Found: C, 75.71; H, 5.92; N, 5.56; S, 12.79.

*Reactions of imines with DPDC.*

*General procedure.* A solution of imine (5 mmol) and DPDC (10 mmol) in benzene (50 mL) was kept at 60 °C until decomposition of the peroxide was complete (4-5 h); the solvent was removed under reduced pressure and the residue chromatographed on silica gel. According to this general procedure the following reactions were carried out.[21]

*Reaction of 1a with DPDC.* **1a** (1.44 g) gave biphenyl (**3**) (0.27 g, 35%), mp = 70-72 °C[22] (from cold light petroleum) and 2-phenylbenzo[d]thiazole (**2a**) (0.67 g, 64%), mp = 112-114 °C (from light petroleum/benzene 70:30 v/v) (lit.[23] mp = 115 °C).

*Reaction of 1b with DPDC.* **1b** (1.62 g) yielded **3** (0.23 g, 30%), mp = 71-72 °C[22] and 2-(4-chlorophenyl)benzo[d]thiazole (**2b**) (0.79 g, 64%), mp = 110-112 °C (from light petroleum/benzene 60:40 v/v) (lit.[24] mp = 112 °C).

*Reaction of 1c with DPDC.* **1c** (1.59 g) afforded **3** (0.25 g, 32%), mp = 70-72 °C[22] and 2-(4-methoxyphenyl)benzo[d]thiazole (**2c**) (0.66 g, 55%), mp = 131-133 °C (from light petroleum/benzene 80:20 v/v) (lit.[25] mp = 134 °C).

*Reaction of 1d with DPDC.* **1d** (1.67 g) gave **3** (0.16 g, 20%), mp = 69-71 °C[22] and 2-(3-nitrophenyl)benzo[d]thiazole (**2d**) (0.63 g, 50%), mp = 186-188 °C (from ethanol) (lit.[26] mp = 186.8-187.3 °C).

*Reaction of 1e with DPDC.* **1e** (1.47 g) yielded **3** (0.12 g, 15%), mp = 70-72 °C[22] and 2-(2-thienyl)benzo[d]thiazole (**2e**) (0.33 g, 30%), mp = 97-99 °C (from light petroleum/benzene 80:20 v/v) (lit.[27] mp = 99.5 °C).

*Reaction of 1f with DPDC.* **1f** (1.69 g) afforded **3** (0.15 g, 20%), mp = 70-72 °C[22] and 2-(2-naphthyl)benzo[d]thiazole (**2f**) (0.65 g, 50%), mp = 127-129 °C (from light petroleum/benzene 70:30 v/v) (lit.[28] mp = 129.5 °C).

*Reaction of 4a with DPDC.* **4a** (1.14 g) gave **2a** (0.18 g, 17%), mp = 112-114 °C (from light petroleum/benzene 70:30 v/v) (lit.[23] mp = 115 °C); benzaldehyde[22] (**5a**) (0.19 g, 35%) and (2-aminophenyl)-thiomethyl *iso*-propyl carbonate (**6**) (0.64 g, 53%), oil which could not be distilled: 60-MHz $^1$H-NMR δ 1.25 (6 H, d, *J* = 6 Hz, -CH-(C*H*$_3$)$_2$), 4.15 (2 H, bs, -N*H*$_2$), 4.85 (1 H, sept., *J* = 6 Hz, -C*H*-(CH$_3$)$_2$), 5.23 (2 H, s, -SC*H*$_2$-), 6.45-6.78 (2 H, m, Ar-*H*), 6.93-7.50 (2 H, m, Ar-*H*); IR $\upsilon_{max}$ 3480, 3380 (-NH$_2$ stretch), 1750 (C=O stretch); MS *m/e* 241 (M$^+$, 55), 138 (37), 137 (17), 136 (18), 125 (100), 124 (19), 43 (47); HRMS calcd for $C_{11}H_{15}NO_3S$ 241.07727, found 241.07681. Anal. calcd for $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; N, 5.80; S, 13.29. Found: C, 54.38; H, 6.22; N, 5.83; S, 13.40.

*Reaction of **4b** with DPDC.* **4b** (1.30 g) yielded **2b** (0.44 g, 36%), mp = 110-112 °C (from light petroleum/benzene 60:40 v/v) (lit.[24] mp = 112 °C); 4-chlorobenzaldehyde (**5b**) (0.34 g, 48%), mp = 49-51 °C[22] (from ethanol) and **6** (0.65 g, 54%).

*Reaction of **4c** with DPDC.* **4c** (1.28 g) afforded **2c** (0.34 g, 28%), mp = 132-134 °C (from light petroleum/ benzene 80:20 v/v) (lit.[25] mp = 134 °C); 4-methoxybenzaldehyde (**5c**) (0.33 g, 48%)[22] and **6** (0.47 g, 39%).

*Reaction of **4d** with DPDC.* **4d** (1.36 g) yielded **2d** (0.48 g, 38%), mp = 186-188 °C (from ethanol) (lit.[26] mp = 186.8-187.3 °C); 3-nitrobenzaldehyde (**5d**) (0.30 g, 40%), mp = 57-59 °C[22] (from ethanol) and **6** (0.42 g, 35%).

*Reaction of **4e** with DPDC.* **4e** (1.16 g) gave **2e** (0.14 g, 13%), mp = 97-99 °C (from light petroleum/ benzene 80:20 v/v) (lit.[27] mp = 99.5 °C); 2-thiophenecarboxaldehyde (**5e**) (0.22 g, 40%)[22] and **6** (0.54 g, 45%).

*Reaction of **4g** with DPDC.* **4g** (1.59 g) afforded **2g** (0.28 g, 24%), mp = 110-112 °C (from light petroleum/benzene 60:40 v/v) (lit.[29] mp = 112 °C); 3-phenyl-2-propenal (**5g**) (0.24 g, 36%)[22] and **6** (0.36 g, 30%).

*Reactions of **1a** with DPDC in chlorobenzene and anisole.* The mixture of the reaction carried out in chlorobenzene was gas-chromatographed affording, by comparison with authentic specimens, 2-, 3-, and 4-chlorobiphenyl in relative yields of 56%, 28%, and 16%, respectively; similarly, for the reaction in anisole solution we obtained 2-, 3-, and 4-methoxybiphenyl in relative yields of 67%, 20%, and 13%.

*Reaction of **4d** with DPDC in the presence of 2,6-di-tert-butylphenol.* **4d** (1.36 g, 5 mmol), DPDC, and 2,6-di-*tert*-butylphenol (6.18 g, 30 mmol) afforded **2d** (0.04 g, 3%), mp = 185-188 °C (from ethanol) (lit.[26] mp = 186.8-187.3 °C); **5d** (0.10 g, 13%), mp = 57-59 °C[22] (from ethanol); **6** (0.12 g, 10%) and [(2-(3-nitrophenyl)methylenamino)phenyl]thiomethyl *iso*-propyl carbonate (**7d**) (0.94 g, 50%), mp = 120-122 °C (from light petroleum/benzene 50:50 v/v):[30] 200-MHz $^1$H-NMR δ 1.30 (6 H, d, $J$ = 5.6 Hz, -CH-(C*H*$_3$)$_2$), 4.92 (1 H, sept., $J$ = 5.6 Hz, -C*H*-(CH$_3$)$_2$), 5.57 (2 H, s, -SC*H*$_2$-), 7.03-7.10 (1 H, m, Ar-*H*), 7.25-7.35 (2 H, m, Ar-*H*), 7.57-7.75 (2 H, m, Ar-*H*), 8.30-8.40 (2 H, m, Ar-*H*), 8.50 (1 H, s, -N=C*H*-), 8.70-8.77 (1 H, m, Ar-*H*); MS *m/e* 374 ($M^+$, 20), 287 (8), 271 (36), 270 (56), 259 (14), 211 (29), 136 (32), 43 (100); HRMS calcd for $C_{18}H_{18}N_2O_5S$ 374.09365, found 374.09325. Anal. calcd for $C_{18}H_{18}N_2O_5S$: C, 57.74; H, 4.85; N, 7.48; S, 8.56. Found: C, 57.49; H, 4.83; N, 7.55; S, 8.63.

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12. Alkoxy radicals are known to abstract the hydrogens of thioanisole to give very low yields of 1,2-bis-(phenylthio)ethane: see ref. 9a and references cited therein.
13. It is worth pointing out that decomposition of DPDC, in benzene at 60 °C, is much faster if carried out in the presence of an imine; therefore, with a radical scavenger, the amount of peroxide available for the non-radical reaction with the methylthio-group might be greater than the quantity which would be left if only a simple unimolecular thermal decomposition of DPDC should occur. An assisted decomposition of DPDC by imidoyl radical was suggested first in: Ohta, H.; Tokumaru, K. *J. Chem. Soc., Chem. Commun.* **1970**, 1601.
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19. The starting materials did not disappear even after 2 days of reflux: the mixture was chromatographed very rapidly on neutral aluminum oxide, eluting with light petroleum/diethyl ether (60:40 v/v).
20. Imines **1e** and **4e** were prepared by keeping overnight a mixture of equimolar amounts of aldehyde and amine at room temperature and under magnetic stirring.
21. In all reactions of imines **1** trace amounts of aldehydes and 2-phenylthiobenzenamine were found as well.
22. Compared with a commercial sample (Aldrich Chemie).
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30. **7d** decomposes slowly at 190 °C and rapidly at 240 °C; a mass spectrum of the final melted mixture showed the presence of high amounts of compound **2d**.