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Studies on the Reaction of Thiocarbonyl-Containing Compounds with Ketenes[1]

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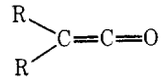
The reactivity of thiocarbonyl-containing compounds with bis(trifluoromethyl)ketene (**1b**) and diphenylketene (**1c**) has been investigated. Replacement of the sulfur atom at the thione position by an oxygen atom was observed for *N*-(diphenylacetyl)-*N'*-carbomethoxyimidazolidinethione (**2a**), 1,3-diethyl-2-thiobarbituric acid (**3a**), and *N*-methylbenzothiazole-2-thione (**4a**) with ketene **1b**. A similar reaction was observed for thione **4a** and *N*-methyl-*N'*-carbomethoxybenzimidazole-2-thione (**10a**) with ketene **1c**. However, treatment of N–H substituted thiones [2-mercaptobenzimidazole (**11a**), 2-mercaptobenzothiazole (**12a**), and *N*-methyl-2-mercaptobenzimidazole (**13a**)] with **1c** led to the formation of 4:1, 2:1, and 1:1 adducts. In these cases, reaction occurred at the nitrogen site. Addition of **1c** to either ethylene trithiocarbonate (**6**) or *N,N*-dimethylthioformamide (**15**) gave the corresponding alkenes **16** and **17** along with COS. Finally, treatment of thiobenzophenone (**7**) and 4,4'-dimethoxythiobenzophenone (**8**) with ketene **1c** gave the corresponding β-thiolactones **20** and **21**, respectively. These two compounds have been incorrectly assigned by previous workers as the isomeric thietanones **23** and **24**.

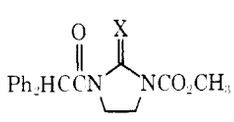
In the preceding paper we reported on the reactivity of acyl-substituted imidazolidones and imidazolidinethiones with ketenes **1a–c**.[3] Significantly, with *N,N'*-disubstituted imidazolidinethiones a novel S→O replacement reaction occurred at the thione position in high yields with ketenes **1b** and **1c**. The reactivity of thiocarbonyl containing compounds with ketenes has not been extensively investigated.[4] We have, therefore, tested the generality of this unique substitution reaction for thiones of varying structure with both **1b** and **1c**.



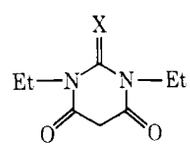
1a, R = H
b, R = CF_3
c, R = Ph

Three types of reactions have been detected. The results of this investigation are reported in the present paper.

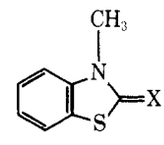
Bis(trifluoromethyl)ketene (1b) Reactions with Thiones. Compounds **2–7** were each treated with 1.1 equiv of ketene **1b**[5] at 60 ± 2 °C. No attempt was made to optimize yields due to the limited supply of the ketene. In only three cases was reaction noted. Thiones **2a**,[3] **3a**, and **4a** gave the S→O replacement products **2b**,[3] **3b**,[6] and **4b**[7] in 100, 43, and 30% yields, respectively. A mechanism similar to the one previously postulated[3] can be drawn for these reactions.



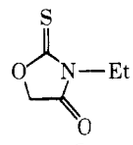
2a, X = S
b, X = O



3a, X = S
b, X = O



4a, X = S
b, X = O



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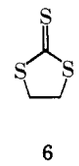

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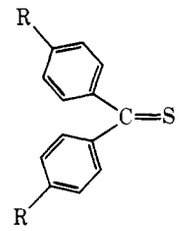
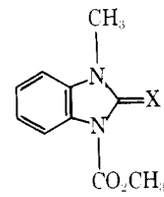


7, R = H
8, R = OMe
9, R = NMe_2



10a, X = S
b, X = O

Diphenylketene (1c) Reactions. The accessibility of diphenylketene[8,9] (**1c**) coupled with our earlier observations[3] prompted us to examine the reactivity of **1c** with a series of thiones. Treatment of *N*-methyl-*N'*-carbomethoxybenzimidazole-2-thione (**10a**) and *N*-methylbenzothiazole-2-thione (**4a**) with **1c** for a period of 4 days at 60 ± 2 °C gave the carbonyl-containing compounds **10b** and **4b**[7] in moderate yield (54 and 20%, respectively). No reaction, however, was detected when thione **5** was treated with **1c**.

When, however, ketene **1c** was added to a thione which contained an active N–H proton flanking the thione group reaction occurred exclusively at the nitrogen site. Treatment of excess **1c** with **11a** and **12a** gave the 4:1 adduct **11b** and the 2:1 adduct **12b** in 74 and 76% yields, respectively. Correspondingly, a mixture of the 2:1 adduct **13b** (43%) as well as the 1:1 adduct **13c** (15%) was observed for the reaction of **13a**[10] with **1c**.

Partial support for the enol acetate structural assignment for these 2:1 and 4:1 adducts stemmed from a favorable comparison of their IR and ^1H NMR spectra with those adducts previously obtained from the reaction of ketene **1c** with imidazolidinethiones.[3] Notable similarities included the tentative assignment of the absorptions at ca. 1760 and 1650

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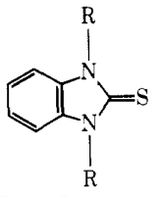
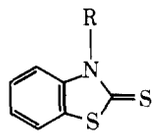
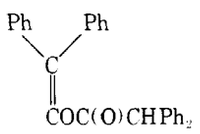


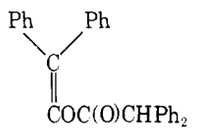
11a, R = H



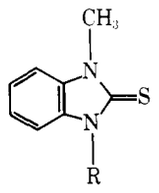
12a, R = H



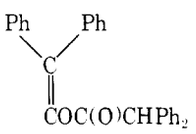
b, R = $COC(O)CHPh_2$



b, R = $COC(O)CHPh_2$



13a, R = H

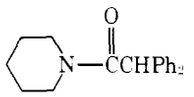


b, R = $COC(O)CHPh_2$

c, R = $C(O)CHPh_2$

cm^{-1} in the IR to the enol ester[11] and the appearance of the downfield singlet in the ^1H NMR at ca. δ 5.05. This absorption can be attributed to the diphenylacetyl methine hydrogen.[3] Furthermore, the UV spectrum for **12b** exhibited a maximum at 336 nm (ϵ 18 600). Koch[12] and D'Amico[13] have shown that an absorption at 328 nm is characteristic for substituted benzothiazole-2-thiones. The UV spectra for the isomeric S-substituted benzothiazoles, on the other hand, typically contained maximas at 275 nm.[12,13]

In addition to the above spectral evidence, compounds **12b**, **13b**, and **13c** each gave a positive spot test for the thione functionality.[14] Finally, treatment of **12b** and **13b** with 1 equiv of piperidine led to the rapid formation of diphenylacetylpiperidine (**14**).[15] In each case, a significant amount of starting



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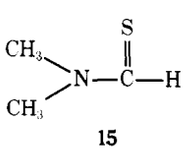
material (**12b** and **13b**) was recovered along with the completely cleaved heterocyclic compound (**12a** and **13a**). These results again appear to be consistent with initial aminolysis of the 2:1 adduct by piperidine to give **14** and the 1:1 adduct, which then is rapidly converted to the N–H thione by piperidine.[3] In a separate control experiment, the 1:1 adduct **13c** underwent rapid (<20 min) aminolysis with piperidine to give **13a** and **14** in high yield.

Surprisingly, the addition of diphenylketene (**1c**) to a CH_2Cl_2 solution containing either ethylenetrithiocarbonate (**6**) or *N,N*-dimethylthioformamide (**15**) gave the corresponding alkenes **16**[16] and **17**[17] in 54 and 69% yields, respectively, along with COS.[18] A reasonable mechanism for the formation of both **16** and **17** involved the initial addition of



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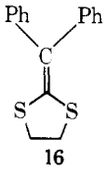

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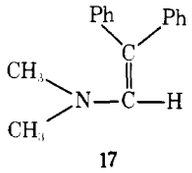

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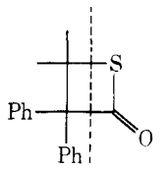
the thione across the carbon–carbon double bond of the ketene to generate the cycloadduct **18**. Ring fragmentation of this adduct would lead to the observed products. Similar mechanisms[4] have been postulated for the initial 1,2-cycloaddition of ketenes with aldehydes,[19] ketones,[19] substituted thiobenzophenones,[20] and isolated carbon–nitrogen double bonds.[20]



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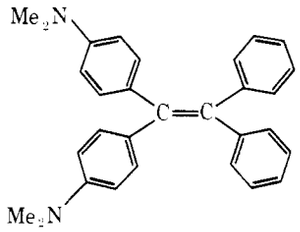
A fourth mode of addition of ketenes to thiones has been reported.[21] In 1920, Staudinger described the reaction of diphenylketene (**1c**) with thiones **7**,[22] **8**,[23] and **9**. Formal addition products were observed in the first two cases, while the ethylene **19** was isolated in the last reaction. The intermediacy



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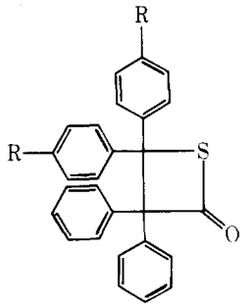
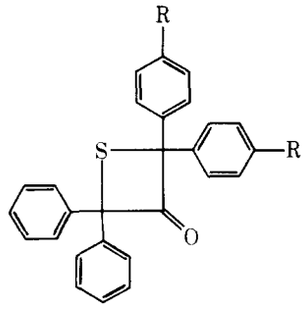
of the β-thiolactone **22** was postulated in the third reaction on the basis of comparable results obtained from the treatment of **1c** with ketones. The inability to observe the extrusion of COS from the first two reaction products to yield the corresponding ethylenes led Staudinger to tentatively propose the 3-thietanone structures **23** and **24** for these adducts. The



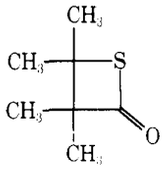
20, R = H
21, R = OMe
22, R = $N(Me)_2$



23, R = H
24, R = OMe
25, R = $N(Me)_2$

isomeric thiolactones (**20** and **21**) as well as alternate structures were not ruled out. Confirmation of the proposed structures by chemical derivatization was hampered by the facile thermal fragmentation of these adducts to the corresponding starting materials.[21] Noteworthy, the formation of thietanones **23** and **24** represents a departure from the normal pattern observed for the reaction of thiones with ketenes. In all the previous examples, the products can be rationalized in terms of initial addition of the thione sulfur to the central atom of the heterocumulene system as opposed to the terminal carbon end.

In 1967, Rioult and Vialle[24] reinvestigated the reaction of **7** with **1c**. The French workers proposed the 3-thietanone structure **23** for the cycloadduct primarily on the basis of the appearance of a carbonyl absorption at 1720 cm^{-1} [25] and the formation of 1,1,3,3-tetraphenylpropanone upon treatment with Ra–Ni. Unfortunately, this band in the infrared spectrum does not insure the proposed structure. Gotthardt has re-



26

ported that the carbonyl frequencies for thiolactone **26** occur at 1757 and 1721 cm^{-1}.[29]

In light of these facts, we have reinvestigated this reaction. Treatment of **1c** with **7** (room temperature, 60 °C, and under conditions identical to those reported by Rioult and Vialle[24]) yielded a compound containing a carbonyl absorption at 1735 cm^{-1}. The structural dilemna (**20** vs. **23**) can simply be resolved by ^{13}C NMR spectroscopy. The symmetry of thioketone **23** demanded a six-line pattern, while an eleven-line spectrum was anticipated for thiolactone **20**. The ^{13}C NMR spectrum for the cycloadduct gave the eleven-line pattern expected for **20**.[30] Furthermore, the chemical shift values obtained for this compound (Figure 1) are in good agreement with the anticipated values for thiolactone **20** as opposed to the thietanone **23**.[31,32] In particular, the appearance of the carbonyl carbon absorption at 194.0 ppm provided compelling evidence for this structural assignment.

In a similar fashion, addition of **8**[23] to **1c** gave the thiolactone **21**. This compound could be obtained as a colorless crystalline material after careful reprecipitation from benzene–hexanes. Noteworthy, compound **21** gave a carbonyl absorption in the infrared spectrum at 1740 cm^{-1} and a twelve-line pattern in the ^{13}C NMR spectrum (Figure 1). Of additional importance was the mass spectrum obtained for **21**. The parent ion could not be observed (EI and CI modes); however, prominent peaks were obtained at *m/e* 258 and 194. These peaks have been assigned to the 4,4′-dimethoxythiobenzophenone and diphenylketene fragments which result from ring cleavage of **21**. Noteworthy, no ions were observed at *m/e* 254 ($(CH_3OC_6H_4)_2CCO^+$) and 198 ($(C_6H_5)_2CS^+$). These additional peaks would have been expected to appear in the mass spectrum, if the thietanone **24** was the correct structure for this adduct.

The identification of the thiolactone structure (**20** and **21**) for the adducts obtained in the last two reactions allows these transformations to be classified together with those reactions previously described for thiones **6** and **15**. In the same vein, this result removes the necessity at this time to invoke yet a fourth mode of addition of thiones to ketenes.[21,22]

Experimental Section

The experimental procedures used in this study are identical to those employed in the previous paper.[3] Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were determined on a Varian Associates Model XL-100-15 spectrometer. The XL-100 was equipped with a Nicolet Technology Corp. TT-100 data system.

Reaction of Substituted Thiones with Bis(trifluoromethyl)ketene (1b). General Procedure. Bis(trifluoromethyl)ketene (**1b**) was transferred from a sealed tube via a standard vacuum line[33] to a cylindrical glass vessel fitted with a Teflon stopcock for storage. A sample of the compound to be treated with the ketene was weighed into a glass vessel (13 × 200 mm) suitable for a sealed tube reaction and then connected to the vacuum line. CH_2Cl_2 (5 mL) was condensed into the reaction tube and then **1b** was measured using a calibrated section of the vacuum line and then vapor transferred to the reaction tube. The vessel was sealed with a torch and then removed to an oil bath maintained at 60 ± 2 °C. After the designated reaction time, the sealed tube was opened and filtered if necessary, and the filtrate was concentrated in vacuo. The residue was then further purified in the manner outlined below to give the observed product(s).

Treatment of *N*-Diphenylacetyl-*N*′-carbomethoxyimidazolidinethione (2a) with Bis(trifluoromethyl)ketene (1b). Using the above procedure **2b** was obtained in quantitative yield after 2 days from **2a** (0.71 g, 2 mmol) and **1b** (0.45 g, 2.5 mmol). Purification was accomplished by reprecipitation from carbon tetrachloride–hexanes: mp 141–142 °C (lit.[3] mp 141–142 °C).

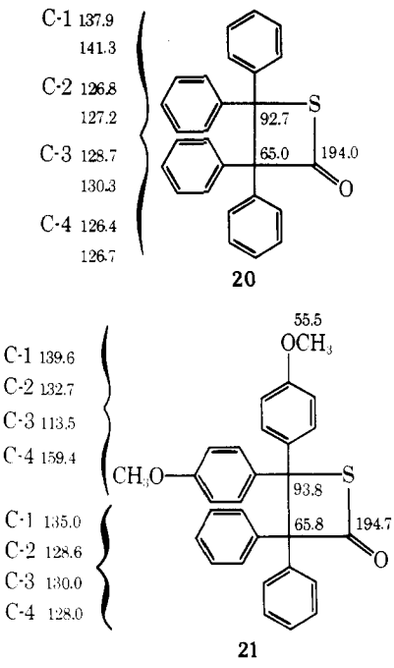


Figure 1.

The white crystalline material which was observed upon completion of the reaction was further dried in vacuo by the removal of solvent and identified as 2,4-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane: yield 0.38 g (100%); mp 84–85 °C (lit.[34] mp 84.5–85.5 °C).

Treatment of 1,3-Diethyl-2-thiobarbituric Acid (3a) with Bis(trifluoromethyl)ketene (1b). Treatment of **3a** (0.40 g, 2 mmol) with **1b** (0.53 g, 3 mmol) according to the above procedure for 1 day gave an oil (0.56 g) which solidified upon standing. The solid was recrystallized from pentane to give **3b**: yield 0.16 g (43%); mp 51–52 °C (lit.[6] mp 52 °C); IR ($CDCl_3$) 1760–1640 (broad) cm^{-1}; NMR ($CDCl_3$) δ 1.05–1.38 (t, *J* = 7.5 Hz, 3 H), 3.70 (s, 1 H), 3.75–4.15 (q, *J* = 7.5 Hz, 2 H); MS *m/e* (rel %) 184 (100), 143 (70), 98 (72), 85 (56), 70 (80), 56 (56); mol wt 184.0822 (calcd for $C_8H_{12}N_2O_3$, 184.0848).

Treatment of *N*-Methylbenzothiazole-2-thione (4a) with Bis(trifluoromethyl)ketene (1b). Utilizing the above procedure, **4b** was obtained after 12 h from **4a** (0.18 g, 1 mmol) and **1b** (0.27 g, 1.5 mmol). The mixture was chromatographed on silica gel (20 g) using CH_2Cl_2 as the eluent. The later fractions yielded 0.05 g (30%) of **4b**: mp 72–74 °C (lit.[7] mp 76 °C); IR 1680 cm^{-1}; NMR ($CDCl_3$) δ 3.40 (s, 3 H), 6.92–7.53 (m, 4 H); MS *m/e* (rel %) 165 (100), 136 (98), 123 (16), 69 (15).

Preparation of *N*-Methyl-*N*′-carbomethoxybenzimidazole-2-thione (10a). NaH (50% mineral oil dispersion) (0.15 g, 3.04 mmol) was washed with DME (3 × 5 mL) and then an additional 20 mL of DME was added. A saturated DME solution of **13a** (0.5 g, 3.05 mmol) was slowly added and then allowed to stir for 1 h. (*N*-Methyl-2-mercaptobenzimidazole (**13a**) (mp 190–191 °C (lit.[10] 187–189 °C)) was prepared in 60% yield according to the method of Tyurenkova, Silina, and Postovskii from *N*-methyl-*o*-phenylenediamine (bp 116–120 °C (8 mm) (lit.[35] bp 116–120 °C (8 mm))). Methyl chloroformate (0.25 mL, 3.17 mmol) was added to the mixture and the reaction was stirred for an additional 15 h. The mixture was filtered, the precipitate thoroughly washed with DME, and the combined DME solutions concentrated in vacuo. The residue was recrystallized from EtOH (2×) to yield 0.61 g of **10a** (90%): mp 156–158 °C; IR (KBr) 1774 cm^{-1}; NMR ($CDCl_3$) δ 3.70 (s, 3 H), 4.12 (s, 3 H), 6.90–7.40 (m, 3 H), 7.60–7.90 (m, 1 H); MS *m/e* (rel %) 222 (100), 177 (17), 163 (24), 149 (17), 145 (70), 132 (20), 131 (27), 119 (73), 100 (16), 92 (17).

Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.54; N, 12.61. Found C, 54.16; H, 4.63; N, 12.55.

Preparation of *N*-Methyl-*N*′-diphenylacetylbenzimidazole-2-thione (13c). The preceding reaction was repeated using 0.37 g (7.68 mmol) of NaH (50% mineral oil dispersion), 1.26 g (7.68 mmol) of **13a**, and 1.77 g (7.68 mmol) of diphenylacetyl chloride[36] (bp 170 °C (13.5 mm) (lit.[36] bp 178 °C (15 mm))). The mixture was concentrated in vacuo, dissolved in CH_2Cl_2 (30 mL), and filtered and then the CH_2Cl_2 layer was washed with a saturated aqueous NaCl solution (50 mL),

dried (Na_2SO_4), and evaporated in vacuo. The residue was triturated with CCl_4 (10 mL), and the remaining solid recrystallized from CCl_4 to give 0.97 g (77%) of the starting material **13a**: mp 190–191 °C (lit.[10] mp 188–189 °C).

The CCl_4 filtrate from the above trituration was concentrated in vacuo and recrystallized from EtOH to yield 0.18 g (6.5%) of **13c**: mp 154–156 °C; IR (KBr) 1720, 1605 cm^{-1}; NMR ($CDCl_3$) δ 3.63 (s, 3 H), 6.83–8.16 (m, 14 H), 8.30 (s, 1 H); MS *m/e* (rel %) 358 (9), 195 (15), 194 (100), 167 (48), 166 (63), 165 (82), 164 (45), 152 (20).

Reaction of Substituted Thiones with Diphenylketene (1c). General Procedure. Diphenylketene (**1c**) was prepared by the thermal decomposition of phenylbenzoyldiazomethane[9] according to the method of Smith and Hoehn:[8] bp 104–105 °C (1.0 mm) (lit.[8] bp 119–121 °C (3.5 mm)).

The substituted thione, **1c**, and CH_2Cl_2 (3–5 mL) were added to a glass tube (13 × 200 mm), sealed with a torch, and then placed in an oil bath maintained at 60 ± 2 °C unless otherwise noted. The vessel was opened after the indicated reaction time, the contents was rinsed with CH_2Cl_2 or acetone and filtered if necessary, and then the filtrate was concentrated in vacuo. The residue obtained was then further purified in the manner outlined below to give the observed products.

Treatment of *N*-Methyl-*N'*-carbomethoxybenzimidazole-2-thione (10a) with Diphenylketene (1c). Treatment of **10a** (0.32 g, 1.4 mmol) with **1c** (0.28 g, 1.4 mmol) according to the above procedure for 4 days gave a mixture upon workup. NMR analysis of the residue indicated only the presence of **8a**, **8b**, and 2,4-bis[1,1-diphenylethylidene]-1,3-dithietane. The solid was chromatographed on a thick-layer silica gel plate using CH_2Cl_2 as the eluent. The first zone (R_f 0.88) collected gave the dithietane: yield 0.15 g (25%); mp 262–263 °C (lit.[37] mp 263 °C).

The second zone (R_f 0.51) was identified as **10a**: yield 0.14 g (44%); mp 156–158 °C.

^1H NMR analysis of the third zone (R_f 0.24) collected indicated the presence of a 90:10 mixture of **10b** and *N*-methylbenzimidazolinone.[38] The sample was further purified by reprecipitation from carbon tetrachloride–hexanes to yield 0.16 g (54%) of **10b**: mp 110–112 °C; IR (KBr) 1795, 1755 cm^{-1}; NMR ($CDCl_3$) δ 3.40 (s, 3 H), 4.08 (s, 3 H), 6.80–7.36 (m, 3 H), 7.80–8.00 (m, 1 H); MS *m/e* (rel %) 206 (100), 162 (20), 161 (15), 147 (42), 119 (51); mol wt 206.0697 (Calcd for $C_{10}H_{10}N_2O_3$, 206.0691).

Treatment of *N*-Methylbenzothiazole-2-thione (4a) with Diphenylketene (1c). Using the above procedure, **4b** was obtained in 20% yield (0.0814 g) after 4 days from **4a** (0.46 g, 2.5 mmol) and **1c** (0.50 g, 2.6 mmol). Purification of the mixture was accomplished by preparative thick-layer silica gel chromatography using CH_2Cl_2 as the eluent. The first zone (R_f 0.82) isolated was identified as 2,4-bis[1,1-diphenylethylidene]-1,3-dithietane: yield 0.10 g (10%); mp 262–263 °C (lit.[37] mp 263 °C).

The second zone (R_f 0.65) gave **4a**: yield 0.36 g (78%); mp 87–89 °C (lit.[39] mp 90 °C).

The last zone (R_f 0.47) collected was reprecipitated from carbon tetrachloride–hexanes and identified as **4b**: yield 0.08 g (20%); mp 75–77 °C (lit.[7] mp 76 °C).

Treatment of 2-Mercaptobenzimidazole (11a) with Diphenylketene (1c). Utilizing the above procedure, **11b** was obtained in 74% yield (2.20 g) from **11a** (0.49 g, 3.2 mmol) and **1c** (2.51 g, 12.9 mmol). The reaction was run at 75 ± 2 °C for 4 days. The product was purified by recrystallization from CCl_4 (2×) and EtOAc: mp 205–207 °C; IR (KBr) 1765, 1650, 1600 cm^{-1}; NMR ($CDCl_3$) δ 5.07 (s, 1 H), 6.33–7.26 (m, 22 H).

Anal. Calcd for $C_{63}H_{46}N_2O_4S$: C, 81.61; H, 5.00; N, 3.02. Found: C, 81.26; H, 5.29; N, 3.08.

Treatment of *N*-Methyl-2-mercaptobenzimidazole (13a) with Diphenylketene (1c). Addition of 0.89 g (4.6 mmol) of **1c** to 0.75 g (4.6 mmol) of **13a** according to the procedure described above (24 h) led to a semisolid residue upon workup. The mixture was triturated with CCl_4 (20 mL) and then the CCl_4 insoluble material was filtered and recrystallized from CCl_4 to yield 0.12 g (16%) of **13a**, mp 190–191 °C (lit.[10] 188–189 °C).

Hexanes (5 mL) were then added to the combined CCl_4 layers and the precipitate formed was collected and then triturated with hexanes (30 mL). The remaining solid was then reprecipitated from carbon tetrachloride–hexanes to yield 0.93 g (37%) of **13b**: mp 169–171 °C; IR (KBr) 1762, 1660 cm^{-1}; NMR ($CDCl_3$) δ 3.56 (s, 3 H), 5.04 (s, 1 H), 6.81–7.40 (m, 24 H); MS *m/e* (rel %) 552 (5), 374 (15), 373 (30), 359 (15), 358 (60), 357 (36), 342 (20), 329 (17), 194 (72), 167 (41), 166 (47), 165 (100), 164 (31).

Anal. Calcd for $C_{36}H_{28}N_2O_2S$: C, 78.23; H, 5.11; N, 5.07. Found: C, 78.31; H, 5.19; N, 5.02.

The carbon tetrachloride–hexanes filtrates were then combined and concentrated in vacuo. NMR analysis of the residue indicated the presence of **13a** (33%), **13b** (18%), and **13c** (49%). The solid was chromatographed on a thick-layer silica gel plate using CH_2Cl_2 as the eluent. Compound **13c** decomposed to the parent thione **13a** on the plate. The first fraction (R_f 0.64) was reprecipitated from carbon tetrachloride–hexanes and identified as **13b**: yield 0.1408 g (6%); mp 169–171 °C.

The second fraction (R_f 0.19) was recrystallized from CCl_4 and identified as **13a**: yield 0.1867 g (24%); mp 190–191 °C (lit.[10] mp 188–189 °C).

Treatment of 2-Mercaptobenzothiazole (12a) with Diphenylketene (1c). Treatment of **12a** (0.50 g, 3.0 mmol) with **1c** (1.29 g, 6.7 mmol) according to the above procedure gave 1.26 g (76%) of **12b**. The reaction was run at 75 ± 2 °C for 4 days. The product was purified by trituration with hot pentane and the remaining solid recrystallized from Et_2O to yield pale yellow crystals: mp 146–149 °C; IR (KBr) 1765, 1650, 1605, 1500 cm^{-1}; UV ($CHCl_3$) 336 (ϵ 18 600), 276 sh (ϵ 14 200), 246 (ϵ 23 900) nm; NMR ($CDCl_3$) δ 5.03 (s, 1 H), 7.00–7.40 (m, 24 H); MS *m/e* (rel %) 555 (1), 361 (1), 360 (2), 332 (2), 195 (17), 194 (100), 167 (46), 166 (44), 165 (80), 152 (10).

Anal. Calcd for $C_{35}H_{25}NO_2S_2$: C, 75.65; H, 4.54; N, 2.52. Found: C, 75.80; H, 4.69; N, 2.55.

Treatment of *N,N*-Dimethylthioformamide (15) with Diphenylketene (1c). Utilizing the above procedure, 1.09 g (5.6 mmol) of **1c** was added to 0.5 g (5.6 mmol) of **15**. The reaction was allowed to proceed for 1 day and then quenched by placing the sealed reaction tube in liquid N_2. The tube was then connected to a U-tube immersed in liquid N_2, the U-tube was evacuated (~15 mm), the reaction vessel was carefully scored and opened, and the formed gases were allowed to vapor transfer to the U-tube by slowly warming the reaction vessel to 0 °C. Analysis of the gas by mass spectrometry identified the presence of carbon oxysulfide: MS *m/e* (rel %) 62 (1.8), 61 (0.3), 60 (18), 44 (100), 32 (15), 28 (78), 16 (41).

NMR analysis of the contents remaining in the original reaction vessel after the workup described above indicated that 69% of the product had been converted to **17**.[17] A sample of **17** was further purified by distillation: bp 85 °C (external temperature) (0.2 mm); mp 83–85 °C (lit.[17] mp 84 °C); IR (KBr) 1620, 1590 cm^{-1}; NMR ($CDCl_3$) δ 2.62 (s, 6 H), 6.34 (s, 1 H), 6.30–7.30 (m, 10 H); MS *m/e* (rel %) 223 (100), 222 (20), 179 (21), 165 (33), 117 (25), 91 (43).

Treatment of Ethylene Trithiocarbonate (6) with Diphenylketene (1c). Addition of 0.50 g (2.6 mmol) of **1c** to 0.25 g (1.8 mmol) of **6** according to the procedure described above gave a 54% yield (0.27 g) of **16**. The reaction was heated for 3 days then quenched in the manner described in the previous experiment. Mass spectrometry indicated the presence of carbon oxysulfide: MS *m/e* (rel %) 62 (3), 61 (1), 60 (63), 44 (39), 32 (28), 28 (100).

The remaining contents in the original vessel were worked-up as described above and the residue chromatographed on a thick-layer silica gel plate using methylene chloride–hexanes (50:50) as the eluent. The first fraction isolated yielded **16**, mp 106–108 °C. This compound could be further purified by sublimation (100 °C, 1.0 mm): IR (KBr) 1600, 1580, 1560, 1530, 1495 cm^{-1}; NMR ($CDCl_3$) δ 3.38 (s, 2 H), 7.32 (s, 5 H); ^{13}C NMR ($CDCl_3$) 38.0, 126.8, 128.0, 129.0, 137.2, 142.9. The remaining quaternary carbon was not detected: MS *m/e* (rel %) 270 (20), 243 (2), 242 (6), 241 (8), 211 (3), 210 (12), 209 (6), 179 (2), 178 (10), 167 (8), 166 (50), 165 (100).

Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.06; H, 5.22; S, 23.72. Found: C, 71.14; H, 5.20; S, 23.78.

The second fraction was identified as **6**: yield 0.09 g (36%); mp 36–37 °C (lit.[40] mp 36–37 °C).

Treatment of Thiobenzophenone (7) with Diphenylketene (1c). Treatment of **7** (0.28 g, 1.4 mmol) with **1c** (0.30 g, 1.5 mmol) according to the above procedure for 3 days gave 0.41 g (74%) of **20**. The product was purified by reprecipitation from chloroform–hexanes and recrystallized twice from $CHCl_3$: mp 182–185 °C dec (lit.[24] mp 185–187 °C); IR (KBr) 1735, 1600 cm^{-1}; IR ($CDCl_3$) 1742, 1600 cm^{-1}; NMR ($CDCl_3$) δ 7.1; MS *m/e* (rel %) 392 (7), 363 (22), 332 (32), 253 (25), 198 (40), 194 (100), 166 (99), 121 (100).

Treatment of 4,4'-Dimethoxythiobenzophenone (8) with Diphenylketene (1c). To an Et_2O solution (10 mL) containing **8** (2.00 g, 7.7 mmol), 1.50 g (7.7 mmol) of **1c** was added. The reaction was stirred at room temperature for 12 h and then the precipitate that formed was collected. The desired compound was purified by reprecipitation from benzene–hexanes to yield 1.20 g of **21** (34%): mp 142–143 °C dec (lit.[21] mp 120 °C); IR (KBr) 1740, 1610 cm^{-1}; IR ($CHCl_3$) 1740, 1610 cm^{-1}; MS *m/e* (rel %) 248 (35), 226 (9), 225 (49), 210 (22), 194 (33), 167 (8), 166 (52), 163 (16), 151 (75), 63 (100), 62 (34).

Treatment of 13b with Piperidine. Freshly distilled piperidine (0.029 mL, 0.290 mmol) was added to a dichloroethane solution (15

mL) containing **13b** (0.16 g, 0.290 mmol). Although the reaction appeared to be complete within 10 min (TLC), it was stirred at room temperature for 15 h. The solution was then concentrated in vacuo and the residue chromatographed on a thick-layer silica gel plate using CH_2Cl_2 as the eluent. The first zone (R_f 0.52) isolated yielded 0.0544 g (34%) after reprecipitation from carbon tetrachloride–hexanes and was identified as starting material **13b**, mp 169–171 °C.

The second fraction (R_f 0.21) isolated was identified as **14**. Reprecipitation from carbon tetrachloride–hexanes gave 0.0780 g (0.280 mmol), mp 117–118 °C (lit.[15] 117–118 °C).

The third zone (R_f 0.08) collected was recrystallized from CCl_4 and identified as **13a**: yield 0.0314 g (66%); mp 190–191 °C (lit.[10] 188–189 °C).

Treatment of 12b with Piperidine. The preceding reaction was run using 0.30 g (0.541 mmol) of **12b** and 0.055 mL (0.553 mmol) of piperidine. The first zone (R_f 0.72) was identified as starting material after reprecipitation from carbon tetrachloride–hexanes: yield 0.1456 g (49%), mp 146–149 °C.

The second fraction (R_f 0.21) (0.2094 g) was shown by NMR to contain an approximate 2:1 mixture of **14** and **12a**.

Treatment of *N*-Methyl-*N'*-diphenylacetylbenzimidazole-2-thione (13c) with Piperidine. Utilizing the above procedure, 0.059 mL (0.59 mmol) of piperidine was added to a dichloroethane solution (5 mL) containing 0.15 g (0.42 mmol) of **13c**. The solution was stirred for 15 h at room temperature although TLC analysis indicated that the reaction was complete within 20 min. The solution was concentrated in vacuo, redissolved in CH_2Cl_2, successively washed with aqueous 5% $NaHCO_3$ (2 × 30 mL) and an aqueous solution of NaCl (2 × 30 mL), and dried (Na_2SO_4). The CH_2Cl_2 was concentrated in vacuo and the remaining residue was chromatographed on a thick-layer silica gel plate using CH_2Cl_2 as the eluent. The first zone (R_f 0.22) collected was identified as **14**. Compound **14** was then reprecipitated from carbon tetrachloride–hexanes to yield 0.0311 g (87%), mp 117–118 °C (lit.[15] mp 117–118 °C).

The second fraction (R_f 0.08) isolated was reprecipitated from carbon tetrachloride–hexanes and identified as **13a**: yield 0.0566 g (82%); mp 190–191 °C (lit.[10] mp 188–189 °C).

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