HCl. The product was collected and dried: 6.2 g (90%). The white powder crystallized from methanol as colorless needles: mp 227–228 °C; IR (KBr) ν_{OH} 2880, ν_{CO} 1730, 1630 cm^{-1}; ^{1}H NMR (unisolv) δ 5.13 (s, 2, CH_2), 8.09–8.60 (m, 5, aromatic); mass spectrum, m/e (% relative intensity) 204 (33) [M$^{+\cdot}$], 159 (100) [M$^{+\cdot}$ – CO_2H].

Anal. Calcd for $C_{10}H_8N_2O_3$: C, 58.83; H, 3.95; N, 13.71. Found: C, 58.86; H, 3.95; N, 13.71.

Dimethyl Pyrrolo[2,1-*a*]phthalazine-1,2-dicarboxylate (18, R = CH_3; R^1 = H). In a flame-dried reaction flask that was flushed with dry N_2, (3,4-dihydro-4-oxophthalizin-3-yl)acetic acid (**17**) (1.0 g, 0.0049 mol), DMAD (0.69 g, 0.0049 mol), and Ac_2O (0.5 g, 0.0049 mol) were refluxed in dry xylene under an atmosphere of dry N_2 for 3–4 h. The xylene was removed by vacuum distillation. Trituration of the residue with anhydrous ether yielded a yellowish powder. Filtration and recrystallization from methanol gave colorless spears: 1.2 g (86%); mp 146–147 °C; IR (KBr) ν_{CO} 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 3, OCH_3), 3.95 (s, 3, OCH_3), 7.5–8.6 (m, 4, aromatic); mass spectrum, m/e (% relative intensity) 284 (100) [M$^{+\cdot}$], 257 (94) (M$^{+\cdot}$ – HCN).

Anal. Calcd for $C_{15}H_{12}N_2O4$: C, 63.38; H, 4.26; N, 9.85. Found: C, 63.29; H, 4.26; N, 9.85.

Similarly, **diethyl pyrrolo[2,1-*a*]phthalazine-1,2-dicarboxylate (18, R = Et; R^1 = H)** was prepared from (3,4-dihydro-4-oxophthalazin-3-yl)acetic acid (**17**) (1.0 g, 0.0049 mol), DEAD (0.83 g, 0.0049 mol), and Ac_2O (0.50 g, 0.0049 mol). It crystallized from ethanol, yielding pale yellow spears: 0.61 g (40%); mp 102–103 °C; IR (KBr) ν_{CO} 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37 (t, 3, J = 7.2 Hz, OCH_2CH_3), 1.42 (t, 3, J = 7.2 Hz, OCH_2CH_3), 4.37 (q, 2, J = 7.2 Hz, OCH_2CH_3), 4.49 (q, 2, J = 7.20 Hz, OCH_2CH_3), 7.24–8.55 (m, 6, aromatic); mass spectrum, m/e (% relative intensity) 312 (100) [M$^{+\cdot}$].

Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.35; H, 5.16; N, 8.97.

Diethyl 3-Phenylpyrrolo[2,1-*a*]phthalazine-1,2-dicarboxylate (18, R = Et; R^1 = Ph). Under reaction conditions analogous to those above, α-phenyl(3,4-dihydro-4-oxophthalazin-3-yl)acetic acid (**12**) (1.0 g, 0.004 mol), DEAD (0.68 g, 0.004 mol), and Ac_2O (0.6 mL, 0.004 mol) were refluxed in dry xylene under an atmosphere of dry N_2 for 6–8 h. On reaction workup the product was recrystallized from ethanol, yielding colorless spears: 1.3 g (85%); mp 114–115 °C; IR (KBr) ν_{CO} 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (t, 3, J = 7.2 Hz, OCH_2CH_3), 1.43 (t, 3, J = 7.2 Hz, OCH_2CH_3), 4.24 (q, 2, J = 7.2 Hz, OCH_2CH_3), 4.47 (q, 2, J = 7.2 Hz, OCH_2CH_3), 7.50–7.83 (m, 8, aromatic), 8.45 (s, 1, C_6-H), 9.0 (m, 1, C_{10}-H); mass spectrum, m/e (% relative intensity) 388 (100) [M$^{+\cdot}$].

Anal. Calcd for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19; N, 7.21. Found: C, 71.09; H, 5.20; N, 7.18.

Acknowledgment. We thank the National Science Foundation for a grant (NSF PCN81-15934) for the purchase of the 200-MHz NMR spectrometer.

Registry No. 1, 16015-46-6; 2, 94392-53-7; 4, 95647-35-1; 6 (R = CN), 95647-36-2; 6 (R = COOEt), 95647-53-3; 7 (X = NEt), 95647-37-3; 7 (X = O), 95647-38-4; 8, 95647-39-5; 9, 95647-40-8; 10, 95647-41-9; 11 (R = H), 82027-00-7; 11 (R = COOEt), 95647-42-0; 11 (R = CO_2H), 95647-44-2; 12 (R = H), 95647-43-1; 12 (R = Et), 95647-45-3; 13, 95647-46-4; 14, 95647-47-5; 15, 95647-48-6; 16, 95647-49-7; 17, 90689-39-7; 18 (R = CH_3, R^1 = H), 95647-50-0; 18 (R = Et, R^1 = H), 95647-51-1; 18 (R = Et, R^1 = Ph), 95647-52-2; DMAD, 762-42-5; DEAD, 762-21-0; PhCHBrCOCl, 19078-72-9; $PhCHBrCO_2H$, 4870-65-9; (*E*)-NCCH=CHCN, 764-42-1; CH_2=CHCOOEt, 140-88-5; HC≡CCOOEt, 623-47-2; PhCHBrCOOEt, 2882-19-1; (*E*)-CH_3OCOCH=CHCOOCH_3, 624-49-7; CH_2=CHCOCH_3, 78-94-4; $BrCH_2CO_2H$, 79-08-3; *N*-ethylmaleimide, 128-53-0; maleic anhydride, 108-31-6; 1(2*H*)-phthalazinone, 119-39-1.

Supplementary Material Available: Selected NMR spectra (1 page). Ordering information is given on any current masthead page.

Photochemistry of the Thioimide Systems: Imide–Thietanes[1]

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General photochemical behavior of cyclic thioimides, nitrogen–thiocarbonyl systems, was studied. The dithioimides were inert to the Norrish type I and II reactions in contrast to the behavior of their oxygen analogues (imides) and nitrogen-lacking counterparts (thiones). However, various aliphatic and aromatic di- and monothioimides underwent intermolecularly efficient photocycloaddition with olefins to afford the imide–thietanes in good yields.

The well-known carbonyl photochemistry has been extended to a nitrogen–carbonyl photochemistry by exploring excited reactivities of the imide system,[2] in which a carbonyl chromophore is in conjunction with an amide group. On the other hand, changing a key element in the ketone chromophore from oxygen to sulfur led to the unique thione photochemistry.[3,4] Obviously a new combination of functional groups leads to a new reactive system, also in excited-state pathways. To develop a frontier of organic photochemistry, we have explored a new amalgamation of such a key chromophore and a kety atom, i.e., imide and sulfur. In the present paper we wish to outline general photochemical behavior of cyclic thioimides, a nitrogen–thiocarbonyl system.

(1) (a) Photochemistry of the Nitrogen–Thiocarbonyl Systems. 2. Part 1: Machida, M.; Oda, K.; Kanaoka, Y. *Tetrahedron Lett.* **1984**, *25*, 409. (b) Photoinduced Reactions. 70. Part 69: Machida, M.; Oda, K.; Kanaoka, Y. *Tetrahedron* in press. (c) A part of this work was preliminarily presented at: 11th Symposium on Organic Sulfur and Phosphorus Chemistry, Tsukuba, Japan, Jan, 1983, Abstracts of Papers, p 125. 9th International Congress of Heterocyclic Chemistry, Tokyo, Japan, Aug, 1983 (proceedings: Oda, K.; Yoshida, E.; Machida, M.; Kanaoka, Y. *Heterocycles* **1983**, *21*, 622).

(2) (a) Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407; (b) Mazzocchi, P. H. "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 421. (c) Machida, M.; Oda, K.; Kanaoka, Y. *Chem. Pharm. Bull.* **1984**, *32*, 75.

(3) (a) de Mayo, P. *Acc. Chem. Res.* **1976**, *9*, 52. Couture, A.; Gómez, J.; de Mayo, P. *J. Org. Chem.* **1981**, *46*, 2010 and many other papers. (b) Ohno, A.; Ohnishi, Y.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1969**, *91*, 5038 and many other papers. (c) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.

(4) Turro, N. J. "Modern Molecular Photochemistry"; The Benjamin/Cummings Publishing Co., Inc.: Menlo Park, CA, 1978; pp 414–472.

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Table I. Photolysis of *N*-Methyldithiosuccinimide (3) in the Presence of Olefins (4a–e)

imide	olefin	time, h	product	yield, %
3	4a, $R^1 = R^2 = R^3 = R^4 = Me$	2.5	5a	83
3	4b, $R^1 = R^2 = R^3 = Me$, $R^4 = H$	2.5	5b	62[a]
3	4c, $R^1 = R^2 = Me$, $R^3 = R^4 = H$	1	5c	58
3	4d, $R^1 = R^3 = Me$, $R^2 = R^4 = H$	1	5d	60[a]
3	4e, $R^1 = OEt$, $R^2 = R^3 = R^4 = H$	2.5	5e	46[a]

[a] A mixture of two stereoisomers.

Results

In the present work dithioimides were generally prepared by employing Lawesson's procedure.[5] Dithiosuccinimides possess a low-intensity band in the UV spectra (EtOH) at around 410 nm ($\epsilon \sim 200$), and a more intensive band near 320 nm ($\epsilon \sim 4 \times 10^4$), assigned to be n,π^* and π,π^*, respectively.[6] First, intramolecular hydrogen abstraction was tested with a series of *N*-alkyldithiosuccinimides **1** and **2**, which were, after irradiation, recovered unchanged quantitatively. This result is in contrast with the facile Norrish type II reaction that occurs with both thiones[3,4] and imides,[2] and suggests either that the excited thioimides are incapable of abstracting hydrogen or that intermediate biradicals, if formed, might readily regenerate the dithioimides (Scheme I).

The possibility of Paterno–Büchi reaction was next examined. *N*-Methyldithiosuccinimide (**3**) underwent photocycloaddition with a series of olefins **4** to give thietanes **5** usually in good yields (Table I). Quantum yield of the formation of **5a** was 0.1, the same order as for the addition of isobutene **4c** to *N*-methylglutarimide.[7]

The structures of all products **5** were determined on the basis of analytical and spectral data. For a typical example, in the mass spectrum of **5a**, the molecular ion peak ($M^+ = 229$) indicated the addition of **4a** to **3**, and the fragment peak with m/z 155 indicated elimination of $S{=}C(Me)_2$ from the thietane **5a**. The ^1H NMR spectrum showed the presence of five methyl groups at 1.15 (CMe × 2), 1.40 (CMe), 1.60 (CMe), and 3.45 (NMe) ppm, respectively. The ^{13}C NMR spectrum showed peaks due to a thiocarbonyl, two dimethyl-substituted carbons, and a quaternary carbon adjacent to a sulfur and a nitrogen atom at 202.1 (s), 57.2 (s), 47.0 (s), and 81.7 (s) ppm, respectively.

Further, photoaddition of dienes was tested. Cyclooctadiene added to **3** giving a mixture of thietane isomers **7** in 75% yield. However, with 2,5-dimethyl-2,4-hexadiene **9**, a triplet quencher, products **10** and **11** were obtained only in poor yields with high recovery of the substrate **3**, an effect suggesting that the reactive state of **3** is triplet. In addition, the formation of **5a** was sensitized in the presence of triphenylene and quenched by the addition of ferrocene.[8] The dithioimide **3** fluoresces very weakly, but has strong phosphorescence, with emission maximum at 478 nm (excited, 328 nm, 77 K; lifetime, 2 ms (in EtOH)), suggesting efficient intersystem crossing. The phosphorescence is quenched by adding ferrocene. For the formation of **5a** the Stern–Volmer plot in degassed benzene (up to 20 mM of ferrocene) is linear with a slope $kq\tau = 25$ M^{-1} (Figure 1). A wavelength-dependence curve of the formation of **5a** was close to the absorption spectrum of the n,π^* transition of **3** (Figure 2).

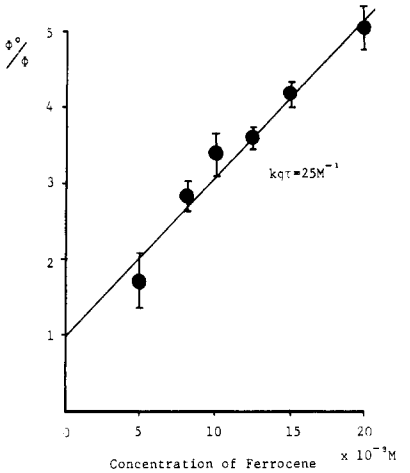


Figure 1. Stern–Volmer plot of thietane **5a** formation: Φ°, quantum yield for formation of thietane **5a** in the absence of a quencher; Φ, quantum yield for formation of thietane **5a** in the presence of a quencher. $kq\tau = 25$ M^{-1}; slope and intercept of Stern–Volmer plots were obtained by least squares of the data.

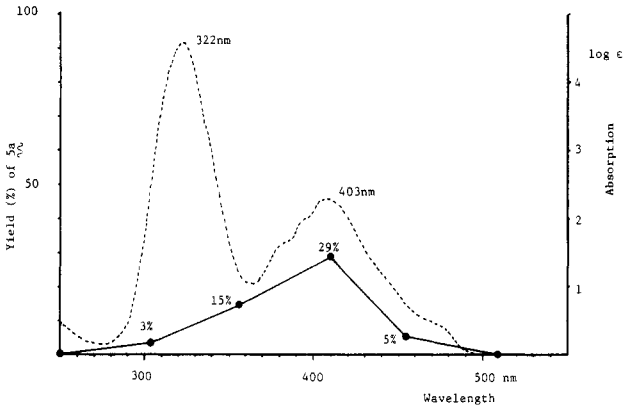


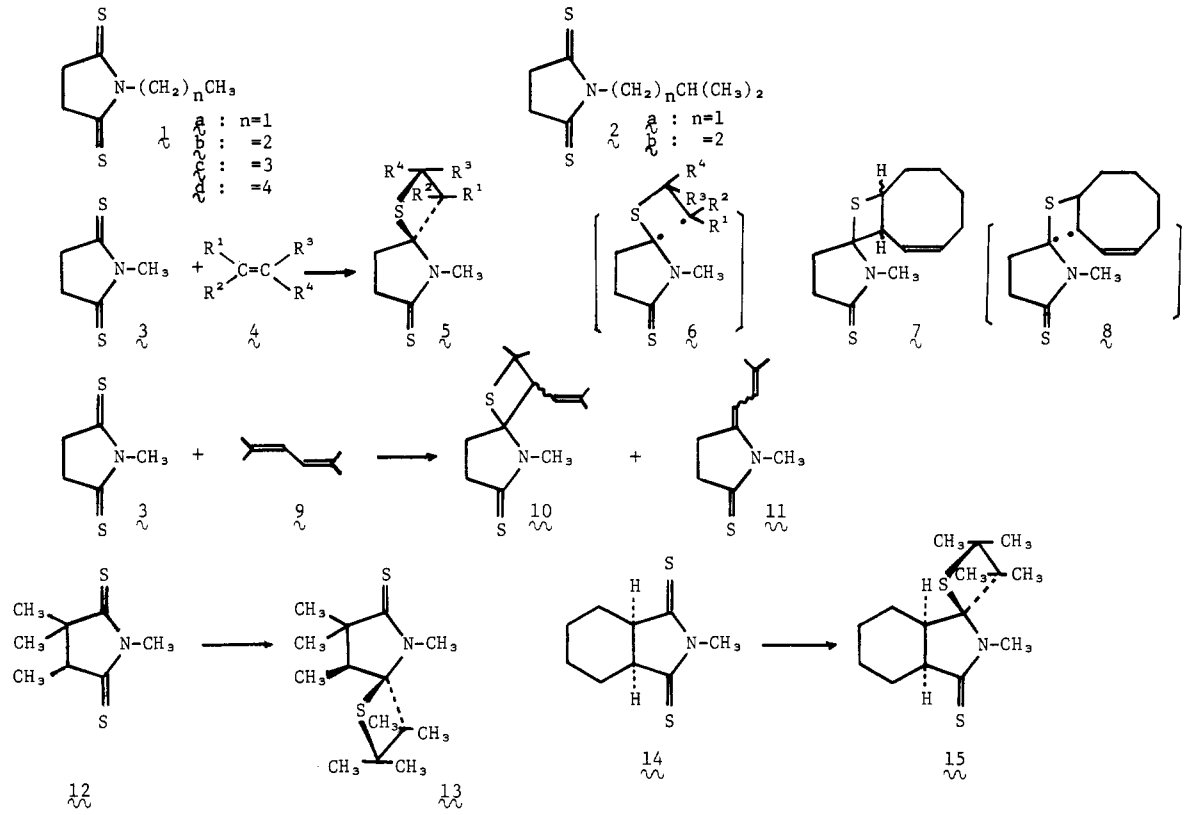
Figure 2. Absorption spectrum and wavelength dependency of the thietane **5a** formation: (···) absorption spectrum of **5a**, (—) yield (%) of thietane **5a**.

Structure of the cyclic thietanes **7** was inferred from the ^1H NMR data of a mixture of stereoisomers. A doublet of doublets appeared at lower field (3.80 and 4.14 ppm) compared with the other methylene signals, indicating the presence of a methine proton adjacent to sulfur atom. Further, this signal of the methine proton was not affected by irradiation of the vinyl protons, suggesting that the methine is not adjacent to the vinyl group. Structural assignments of the photoproducts **10** and **11** were made on the basis of spectroscopic data and the conversion of **10** to **11** which was identified by the ^1H NMR spectrum. The ^1H NMR spectrum of **10** showed the presence of five methyl group and one vinyl proton. In the mass spectrum of **10**, a fragment peak with m/z 181 indicated elimination of $S{=}C(Me)_2$ from the molecular ion, suggesting that geminal methyl groups are attached to the carbon adjacent to sulfur in the thietane ring. The ^1H and ^{13}C NMR spectra of **11** indicated the presence of three methyl groups and four olefinic carbons. Compound **11** was easily obtained from the photolysate of **10**, a result confirming that **11** is a secondary photoproduct from **10**.

When the dithiosuccinimide was unsymmetrically substituted as in **12**, the less-hindered thiocarbonyl was regioselectively attacked (**13**, 58%). The stereochemistry of **13** was inferred by assuming the addition of **4a** from the less hindered side of the thiocarbonyl. We have previously reported that with the similarly substituted succinimides, α-cleavage between the imide carbonyl and the more

(5) Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.
(6) Bergand, U.; Sandström, J. *Acta Chem. Scand.* **1966**, *20*, 689.
(7) Kanaoka, Y.; Yoshida, K.; Hatanaka, Y. *J. Org. Chem.* **1979**, *44*, 664.
(8) de Mayo, P.; Syndes, L. K.; Wenska, G. *J. Org. Chem.* **1980**, *45*, 1549.

Scheme I



substituted α-carbon is predominant over other reactions leading to rearrangement reactions.[9] Therefore the above result indicates that Norrish type I process is not important in this thioimide system. Irradiation of cis-bicyclic thiosuccinimide **14** in the presence of **4a** afforded only the *cis*-thietane **15** (32%), and from the recovered material no isomerized trans substrate was detected,[10] again indicating that the α-cleavage is never significant in the thioimide system.

Reactions of the aromatic cyclic thioimides were studied under similar conditions. Again, none of *N*-alkyldithiophthalimides **16** showed hydrogen-abstracting ability. As expected, cycloaddition of **4a** to **17** took place to give a thietane **18** (43%) accompanied by an unsaturated product **19** (10%). The mass spectrum of **18** showed the molecular ion peak at m/z 277 and a characteristic fragment peak (m/z 203) corresponding to the loss of S=C-$(Me)_2$ from the molecular ion. The ^1H NMR spectrum showed the presence of five methyl groups at 1.00, 1.25, 1.70 (2Me), and 3.80 (NMe) ppm. In the mass spectrum of **19**, the molecular ion peak was observed at m/z 203 corresponding to the fragment peak of **18**. ^1H and ^{13}C NMR spectra showed the presence of three methyl groups and newly formed two olefinic carbons: 2.40 (s, 2Me), 3.95 (s, NMe) ppm; 131.6 (s), 132.8 (s) ppm. Formation of the unsaturated thioamide **19** may be explained by a subsequent photolysis of the initially formed **18**, indicative of promoted photoreactivity of the aromatic imide–thietanes relative to the aliphatic ones, due to a favored formation of the benzylic radical intermediate **20**. In the presence of the diene **9**, the reaction gave thietanes **21** (42%) and again the photolyzed products **22** (18%) as mixtures of two inseparable stereoisomers. A plausible intermediate **20** to **22** from **21** is a biradical stabilized by double conjugation with phenyl and vinyl groups (Scheme II).

In order to gain more information about the role of the sulfur atom in the thioimides with respect to the corresponding imide system, behavior of monothioimides was studied. Photoreactions of *N*-methylthiosuccinimide (**23**) with **4a** gave the thietane **24** in preference to the oxetane **25**, in 32% and 10% yields, respectively, reflecting the enhanced reactivity of the thiocarbonyl relative to the imide carbonyl (Scheme III).

With the aromatic counterpart, *N*-methylmonothiophthalimide **26**, irradiation in the presence of **4a** gave rise to only the thietane **27** (60%), a product from the reaction with the thiocarbonyl moiety, and none of the corresponding oxetane was isolated. Product **27** showed characteristic signals in its NMR and mass spectra: ^1H NMR δ 1.00 (s, Me), 1.20 (s, Me), 1.65 (s, 2Me), 3.40 (s, NMe); ^{13}C NMR δ 47.4 (s, S*C*$(Me)_2$), 57.2 (s, *C*$(Me)_2$), 81.5 (s, SCN), 164.8 (s, C=O); mass spectrum, m/z 261 (M^+), 187 (M^+ - S=C$(Me)_2$). When stilbene **28** was used as an olefin component, **26** afforded two stereoisomers of the thietanes (**29a**, 36%; **29b**, 44%), which could be easily discriminated from each other by the chemical shifts of NMe protons (3.00 ppm for **29a** and 3.45 ppm for **29b**) due to anisotropic effects of the phenyl ring, which is more close to the NMe in **29a** than in **29b**.

Discussion

From the above results it is evident that the photochemistry of the thioimides is dominated by cycloaddition or Paterno–Büchi reaction. Thietane formation is a well-known typical reaction of thiones,[3] and biradical intermediates commonly accepted in the thione photo-

(9) Kanaoka, Y.; Okajima, H.; Hatanaka, Y. *J. Org. Chem.* **1979**, *44*, 1749.

(10) In the analogous imide system, α-cleavage of the **12** analogue led to a mixture with the trans isomers.[9] In the thione photochemistry, α-cleavage is not well documented, although special examples were reported with thiolactones[11a] and thiocyclobutanediones.[11b]

(11) (a) Muthuramu, K.; Ramamurthy, V. *J. Chem. Soc., Chem. Commun.* **1980**, 234. (b) Muthuramu, K.; Ramamurthy, V. *J. Org. Chem.* **1980**, *45*, 4533.

Scheme II

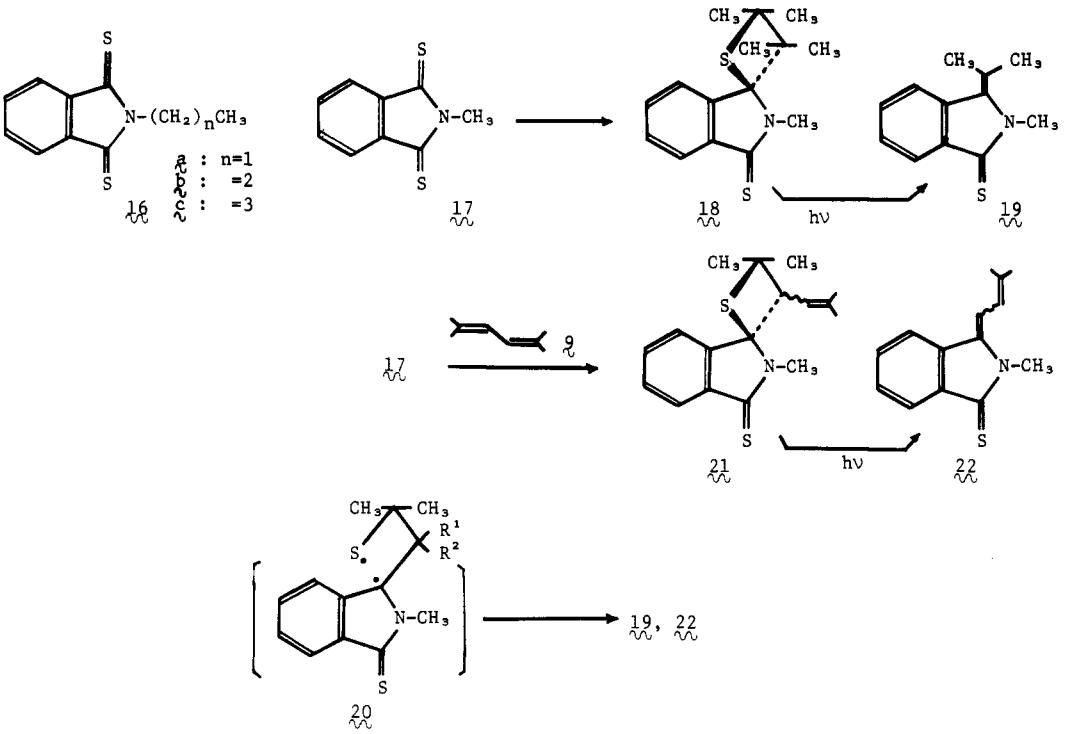


Table II. Comparison of Photoreactivities of the Nitrogen–Carbonyl and the Nitrogen–Thiocarbonyl Systems[a]

	ketone	amide	imide	thioketone	thioamide	thioimide
Norrish type I	+	+	+	(+)	–	(–)
Norrish type II	+	–	+	+	–	(+)
cycloaddition	+	–	+	+	(+)	+

[a] (+) Reactive, (–) unreactive.

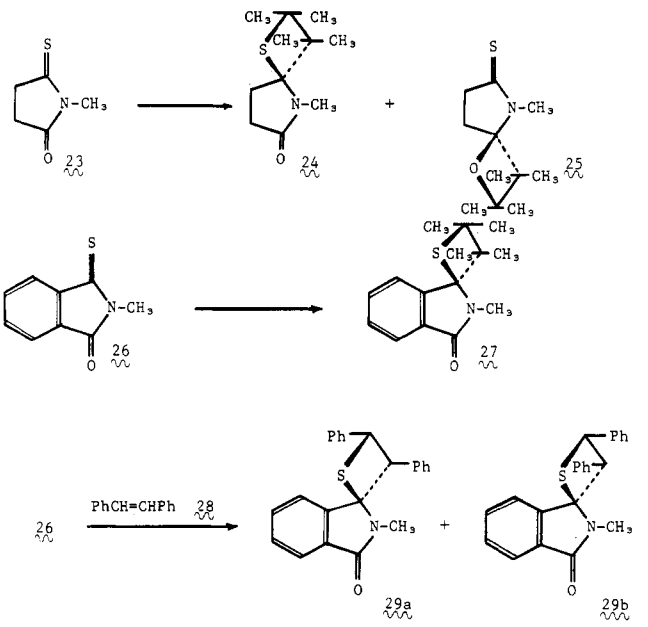
chemistry are also assumed for the pathways of the cycloaddition of thioimides. The product distribution shown in Table I is in agreement with this assumption in terms of the involvement of the biradical **6**. Structure **7** is also consistent with this assumption of a more stable radical intermediate **6** since a vinyl biradical **8** is a reasonable intermediate for the formation of **7**. On the basis of the data of the quenching (Figure 1) and the wavelength-dependence experiments (Figure 2), the cycloaddition of **3**, initiated by n,π^* excitation, has all the appearance of being a triplet process. Although it is well-known that excited thiones have ability to give products derived from reaction of a higher singlet state,[3a] there are no indications of the involvement of the higher states in the reactions of thioimides in view of the wavelength dependency.

With respect to the construction of photoreactive systems by combining chromophore units, it has been shown that, in going from ketone to imide by way of amide, the effects of nitrogen and one carbonyl appear to compensate each other, and in a simple approximation, imides resemble their parent ketones.[2a] Thus the photochemical behavior of imides parallels in many ways that of ketones as briefly summarized in Table II.

In this regard it is worth noting that the thioimides seem unusually inert to Norrish type I and II processes in contrast to the behavior of their oxygen analogues (imides) and nitrogen-lacking counterparts (thiones) (Table II). In the mechanistic studies of hydrogen abstraction of aralkyl thiones, Ho and de Mayo reported that only about one-tenth of the biradicals cyclize and the rest disproportionate to give the original thione.[12] To ascertain whether the

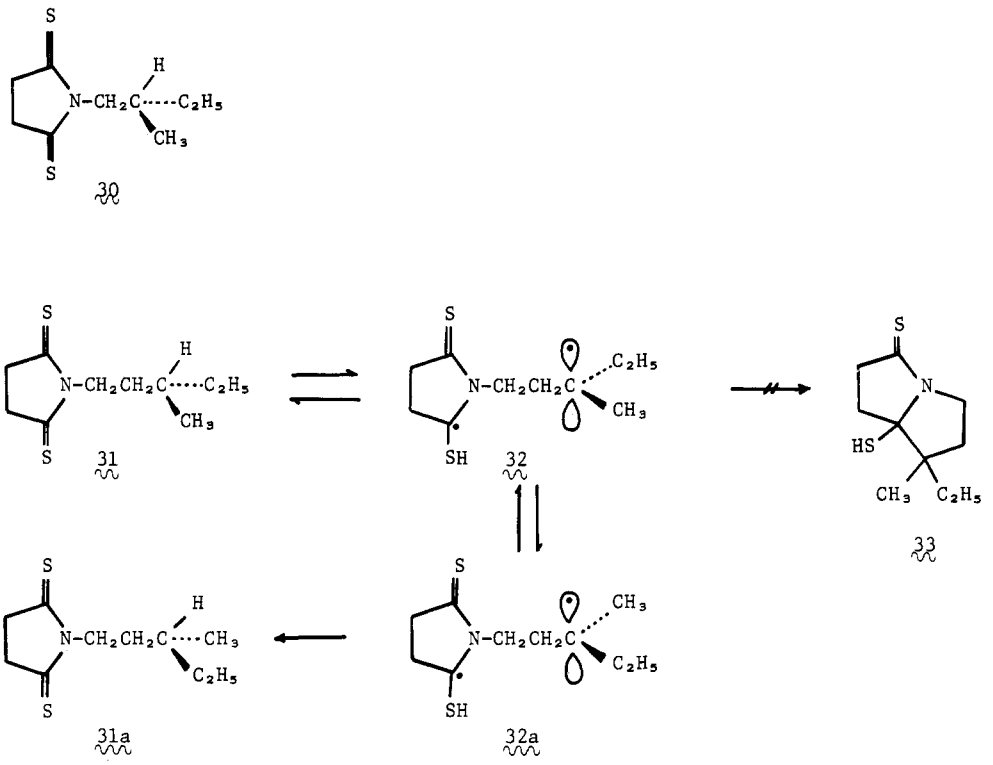
(12) Ho, K. W.; de Mayo, P. *J. Am. Chem. Soc.* **1979**, *101*, 5727.

Scheme III



thiocarbonyl of *N*-alkylsuccinimides is truly unreactive or actually abstracts a hydrogen but only returns to the starting thioimide, **30** and **31** were synthesized. Succinimide was alkylated at the nitrogen with the chiral alkyl bromide, and the *N*-alkylsuccinimide was converted to the dithiosuccinimide by treating with Lawesson reagent.[5] When dithioimide **30** asymmetrically substituted at the γ-position was irradiated in benzene, no photoracemization was observed. However, with **31**, the dithioimide asym-

Scheme IV



metrically substituted at the δ-position, racemization took place on irradiation. This result seems reasonable because in some thione series, in contrast to that of ketones,[13] the δ C–H abstraction (through the S_2 state[3a]) is preferred to the γ C–H, although the latter is definitely reactive in the normal carbonyl photochemistry. There may exist an intermediate biradical **32** which is slow in cyclization to form the product **33** but lives long enough to lose its configurational integrity at the δ-carbon **32a**, which returns to a ground state of the enantiomeric thioimide **31a**. The apparent inertness of the dithioimides to the Norrish type II reaction is, at least in part, explained by the disproportionation of the biradical back to the starting material (Scheme IV).

It is interesting that from the reaction of **26** and **28** only the trans isomers **29** were obtained among four possible thietane products, through under the irradiation conditions photoepimerization of **28** to *cis*-stilbene seems possible. Presumably photoequilibrium between the products would have resulted in the favored distribution of the two trans isomers. In view of the above and other observation of the secondary photolysis leading to unsaturated thioamides **11**, **19**, and **22**, photochemical behavior of imide–thietanes as well as their thermal behavior remains for further study.

In conclusion, the excited thioimide function has distinctive characteristics: aliphatic and aromatic cyclic dithioimides undergo exclusively photocycloaddition with olefins. The other reactions common to the parent thione and imide family are not important, and consequently little side reaction occurs. For example, with substrates having γ- and δ-hydrogens, no photocyclization will be a competitive reaction. Even with increasing substitution α to the thiocarbonyl, neither α-cleavage nor the subsequent rearrangements are competitive. Imide–thietanes, directly produced by this reaction, are a spiro system containing both sulfur and nitrogen otherwise unaccessible, and have structural features as interesting intermediates for various reactions since the thietane system may be involved in varied fission and recombination transformations. Thus the photocycloaddition of thioimides may provide a synthetic entry to new nitrogen- and sulfur-containing heterocyclic systems. Application of this method, including synthesis of highly strained multicyclic sulfur- and nitrogen-containing systems, is under way.

(13) Reference 4, pp 386–392.

Experimental Section

Melting points were measured on a Yamato melting point apparatus (Model MP-21) and are uncorrected. IR spectra were recorded on a Shimadzu IR-400 spectrometer. NMR spectra were taken on a Hitachi R-40 spectrometer and a JEOL-FX 60 spectrometer or a JEOL-JNM-FX 90Q spectrometer. The chemical shifts are reported in δ values relative to tetramethylsilane, which was used as internal standard. Mass spectra were obtained on a JEOL JMS-QH 100 mass spectrometer. Ultraviolet absorption (UV) spectra were measured with a Hitachi 228 spectrophotometer. Emission spectra were measured with a Hitachi 650-60 fluorescence spectrophotometer equipped with a Hitachi phosphoroscope attachment (650-0175). Preparative irradiations were conducted by using a 1 kW high-pressure mercury lamp (Eikosha EHB-W-1000) through Pyrex glass at room temperature. Stirring of the reaction mixture was effected by the introduction of a stream of nitrogen at the bottom of the outer jacket. Wavelength-dependence experiments were carried out a JASCO CRM-FA spectroirradiator. Quantum yield measurements and quenching experiments were carried out with a 500-W high-pressure mercury lamp (Eikosha PIH 500). All column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70–230 mesh). Gas chromatographic analyses were performed on a Hitachi 163 gas chromatograph equipped with a flame ionization detector using a 2 m × 3 mm, 1.5% OV-17 on Chromosorb W (60–80 mesh), glass column.

General Procedure for Preparations of *N*-Alkyldithiosuccinimides 1 and 2 and *N*-Alkylthiophthalimides 16, 17, and 26. *N*-Alkylthioimides were prepared from the corresponding imide following the procedure of Lawesson et al.[5] Monothioimides and dithioimides were isolated from the reaction mixture by column chromatography on silica gel.

1a: yield, 52%; bp 180–184 °C (16 mm). Anal. Calcd for $C_6H_9NS_2$: C, 45.28; H, 5.70; N, 8.80. Found: C, 45.44; H, 5.68; N, 8.92.

1b: yield, 56%; bp 161–163 °C (12 mm). Anal. Calcd for $C_7H_{11}NS_2$: C, 48.55; H, 6.40; N, 8.09. Found: C, 48.51; H, 6.67; N, 8.16.

1c: yield, 61%; bp 128–130 °C (10 mm). Anal. Calcd for $C_8H_{13}NS_2$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.21; H, 7.13; N, 7.44.

1d: yield, 53%; bp 145–148 °C (15 mm). Anal. Calcd for $C_9H_{15}NS_2$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.65; H, 7.28; N, 6.81.

2a: yield, 59%; bp 162–166 °C (18 mm). Anal. Calcd for $C_8H_{13}NS_2$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.21; H, 6.89; N, 7.55.

2b: yield, 56%; bp 144–146 °C (12 mm). Anal. Calcd for $C_9H_{15}NS_2$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.61; H, 7.70; N, 6.81.

16a: yield, 48%; mp 81–83 °C (hexane). Anal. Calcd for $C_{10}H_9NS_2$: C, 57.97; H, 4.38; N, 6.76; S, 30.89. Found: C, 57.81; H, 4.43; N, 6.65; S, 30.91.

16b: yield, 59%; mp 75–76 °C (hexane). Anal. Calcd for $C_{11}H_{11}NS_2$: C, 59.72; H, 5.01; N, 6.33; S, 28.93. Found: C, 59.86; H, 5.13; N, 6.45; S, 28.79.

16c: yield, 46%; mp 73–76 °C (hexane). Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.27; H, 5.57; N, 5.96; S, 27.27. Found: C, 61.33; H, 5.48; N, 6.01; S, 27.34.

17: yield, 48%; mp 91–92 °C. Anal. Calcd for $C_9H_7NS_2$: C, 55.96; H, 3.65; N, 7.25; S, 33.13. Found: C, 56.08; H, 3.59; N, 7.33; S, 33.24.

26: yield, 31%; mp 86–87 °C (lit.[14] mp 97 °C). Anal. Calcd for C_9H_7NOS: C, 61.00; H, 3.89; N, 7.90; S, 18.09. Found: C, 60.84; H, 4.00; N, 7.87; S, 18.20.

Preparation of *N*-Methylthiosuccinimides 3 and 23. Thiosuccinimides were prepared from *N*-methylsuccinimide and phosphorus pentasulfide following the procedure of Bergand and Sandström,[6] and separation by column chromatography gave **3** and **23** in 68% and 20% yields, respectively. **3**, mp 108–110 °C (lit.[6] mp 112–113 °C); **23**, mp 58–60 °C (lit.[6] mp 59–60 °C).

Preparation of *cis*-*N*-Methylcyclohexane-1,2-dithiocarboximide (14). *cis*-*N*-Methylcyclohexane-1,2-dicarboximide was prepared by fusion of a mixture of 1,2-cyclohexanedicarboxylic anhydride and methylamine in an usual manner, mp 68–69 °C (EtOH). A solution of the imide (0.01 mol) and Lawesson reagent (0.01 mol) in benzene was refluxed for 5 h. After removal of the solvent, the residue was chromatographed over silica gel to give **14**, bp 162–165 °C (18 mm). Anal. Calcd for $C_9H_{13}NS_2$: C, 54.26; H, 6.58; N, 7.03; S, 32.13. Found: C, 54.22; H, 6.70; N, 7.01; S, 32.30.

Preparation of 1,3,3,4-Tetramethyldithiosuccinimide 12. Ethyl 2,3-dicyano-2,3,3-trimethylpropionate, prepared from ethyl 2-cyano-3,3-dimethylacrylate, potassium cyanide, and methyl iodide, was hydrolyzed to give 2,3,3-trimethylsuccinic acid, mp 114–116 °C (lit.[15] mp 114–116 °C). A mixture of 2,3,3-trimethylsuccinic acid and 40% methylamine aqueous solution was heated at 150 °C in the usual manner, and the crude product was purified by column chromatography on silica gel to give 1,3,3,4-tetramethylsuccinimide, mp 68–70 °C. Next, a solution of the resulting imide (0.01 mol) and Lawesson reagent (0.01 mol) in benzene was refluxed for 5 h. After removal of the solvent the residue was chromatographed over silica gel to afford **12** in 73% yield, bp 158–161 °C (10 mm). Anal. Calcd for $C_8H_{13}NS_2$: C, 51.33; H, 7.00; N, 7.48; S, 34.19. Found: C, 51.27; H, 7.04; N, 7.33; S, 34.31.

Preparation of Asymmetrically Substituted Dithiosuccinimides 30 and 31. (*S*)-(+)-1-Bromo-2-methylbutane and (*S*)-(+)-1-bromo-3-methylpentane were prepared according to the reported procedure.[16] A mixture of (*S*)-(+)-1-bromo-2-methylbutane, succinimide, and potassium carbonate was warmed under stirring at 70 °C for 15 h. After removal of the solvent the crude product was chromatographed over silica gel to afford the succinimide derivative. A solution of the succinimide and Lawesson reagent in benzene was then refluxed for 5 h, and separation by column chromatography gave the corresponding dithiosuccinimide **30** in 42% yield, bp 139–141 °C (15 mm), $[\alpha]^{20}_D$ −3.96° (10 mM CH_3CN). Anal. Calcd for $C_9H_{15}NS_2$: C, 53.72; H, 7.51; N, 6.96; S, 31.81. Found: C, 53.84; H, 7.56; N, 7.08; S, 31.69.

Dithiosuccinimide Derivative 31. Dithioimide **31** was prepared as described above: yield, 51%; bp 151–155 °C (17 mm); $[\alpha]^{20}_D$ −7.63° (10 mM CH_3CN). Anal. Calcd for $C_{10}H_{17}NS_2$: C, 55.80; H, 7.96; N, 6.51; S, 29.73. Found: C, 55.78; H, 7.89; N, 6.68; S, 29.77.

Irradiation of *N*-Alkyldithiosuccinimides 1 and 2. A solution of *N*-alkyldithiosuccinimide (5 mmol) in benzene (500 mL) was irradiated at room temperature for 20 h. The unreacted dithiosuccinimides were recovered quantitatively by column chromatography on silica gel.

Irradiation of *N*-Methyldithiosuccinimide (3) in the Presence of Olefins 4a–e. Formation of Thietanes 5. A solution of *N*-methyldithiosuccinimide **3** (5 mmol) and olefin **4** (25 mmol) in 500 mL of benzene was irradiated for 1–2.5 h. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel column and the photoproducts **5a,c** were purified by recrystallization, but the other thietanes (**5b,d,e**) were obtained as 1:1 mixtures of two inseparable stereoisomers.

5a: mp 114–115 °C (ethyl acetate); MS, *m/z* 229 (M^+), 155 (M^+ − S=C(Me)$_2$); ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 6 H, Me × 2), 1.40 (s, 3 H, Me), 1.60 (s, 3 H, Me), 2.0–3.2 (m, 4 H), 3.45 (s, 3H, NMe); ^{13}C NMR ($CDCl_3$) δ 202.0 (s), 81.7 (s), 57.2 (s), 47.0 (s), 37.2 (t), 35.9 (q), 35.8 (t), 30.1 (q), 27.0 (q), 23.7 (q), 23.0 (q). Anal. Calcd for $C_{11}H_{19}NS_2$: C, 57.59; H, 8.35; N, 6.11; S, 27.96. Found: C, 57.70; H, 8.42; N, 5.81; S, 28.20.

5b: MS, *m/z* 215 (M^+), 155 (M^+ − S=CHMe); ^{1}H NMR ($CDCl_3$) δ 0.95, 1.10 (2 s, 3 H, Me), 1.20, 1.30 (2 s, 3 H, Me), 1.20, 1.30 (2 d, *J* = 6, 7 Hz, 3 H, Me), 1.7–3.0, 2.0–3.2 (2 m, 4 H), 3.30, 3.60 (2 q, *J* = 7, 6 Hz, 1 H, C*H*Me), 3.45, 3.60 (2 s, 3 H, NMe).

5c: mp 82–84 °C (hexane); MS, *m/z* 201 (M^+), 127 (M^+ − S=C(Me)$_2$); ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 3 H, Me), 1.45 (s, 3 H, Me), 1.7–3.0 (m, 4 H), 2.55 (d, *J* = 12 Hz, 1 H), 3.05 (d, *J* = 12 Hz, 1 H), 3.85 (s, 3 H, NMe); ^{13}C NMR ($CDCl_3$) δ 201.8 (s), 87.1 (s), 52.2 (s), 42.1 (s), 35.3 (t), 34.9 (t), 33.4 (q), 28.5 (q), 25.6 (q). Anal. Calcd for $C_9H_{15}NS_2$: C, 53.72; H, 7.51; N, 6.96; S, 31.81. Found: C, 53.88; H, 7.46; N, 6.88; S, 31.88.

5d: MS, *m/z* 201 (M^+), 141 (M^+ − S=CHMe); ^{1}H NMR ($CDCl_3$) δ 1.00, 1.05 (2 d, *J* = 7 Hz, 3 H, Me), 1.40, 1.45 (2 d, *J* = 7 Hz, 3 H, Me), 1.5–3.5, 2.0–3.5 (2 m, 6 H), 3.35, 3.55 (2 s, 3 H, NMe).

5e: MS, *m/z* 217 (M^+), 171 (M^+ − S=CH_2); ^{1}H NMR ($CDCl_3$) δ 0.90, 0.95 (2 t, *J* = 7 Hz, 3 H, CMe), 2.5–3.2 (m, 16 H), 3.30, 3.55 (2 s, 3 H, NMe), 3.75, 4.60 (2 t, *J* = 7, 8 Hz, 1 H, C*H*OC_2H_5).

Irradiation of *N*-Methyldithiosuccinimide (3) with Conjugated Dienes, Cyclooctadiene, and 2,5-Dimethyl-2,4-hexadiene (9). (A) Irradiation in the Presence of Cyclooctadiene. A solution of **3** (1.5 g, 0.01 mol) and cyclooctadiene (5 g, 0.05 mol) in 500 mL of benzene was irradiated for 0.5 h. Workup of the reaction mixture in the usual manner gave **7** in 75% yield as a 1:1 mixture of stereoisomers. **7**: MS, *m/z* 253 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.0–3.2 (m, 13 H), 3.35, 3.60 (2 s, 3 H, NMe), 3.80, 4.15 (2 dd, *J* = 10, 4 Hz, 1 H, SCH), 5.2–5.9 (m, 2 H, vinyl H).

(B) Irradiation in the Presence of 9. A solution of **3** (0.01 mol) and **9** (0.05 mol) in 500 mL of benzene was irradiated for 7.5 h. Workup of the mixture gave thietane **10** and unsaturated thioamide **11** in 6% and 3% yields, respectively, accompanied by the unchanged starting material (**3**) (82%). Each photoproduct was obtained as a 1:1 mixture of stereoisomers.

10: MS, *m/z* 255 (M^+), 181 (M^+ − S=C(Me)$_2$); ^{1}H NMR ($CDCl_3$) δ 1.10 1.15, 1.20, 1.25 (4 s, 6 H, 2Me), 1.95, 2.05 (2 s, 6 H, C=C(Me)$_2$), 2.4–2.9 (m, 4 H), 3.10, 3.15 (2 d, *J* = 7 Hz, CHC=C), 3.45, 3.55 (2 s, 3 H, NMe), 6.45, 6.35 (2 d, *J* = 7 Hz, 1 H, CH=C).

11: MS, *m/z* 181 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.85, 2.15, 1.90, 2.10 (1:1.4, 4 s, 6 H, C=C(Me)$_2$), 2.3–2.8 (m, 4 H), 3.45, 3.50 (1:1.4, 2 s, NMe), 6.4–6.8 (m, 2 H, vinyl H).

Irradiation of 12 in the Presence of 4a. Formation of Thietane 13. A solution of **12** (5 mmol) and **4a** (25 mmol) in benzene was irradiated for 2 h as described above. Workup of the reaction mixture gave **13** in 58% yield as the only product, and 23% of the starting material **12** could be recovered unchanged.

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(15) Moal, H. L.; Foucaud, A.; Carrie, R.; Robert, A.; Danion, D. *Bull. Soc. Chim. Fr.* **1964**, 2553.
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13: mp 81–83 °C; MS, m/z 271 (M^+), 197 ($M^+ - S{=}C(Me)_2$); ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 7 Hz, 3 H, Me), 1.10 (s, 6 H, Me × 2), 1.20 (s, 3 H, Me), 1.25 (s, 3 H, Me), 1.35 (s, 3 H, Me), 1.40 (s, 3 H, Me), 2.55 (q, J = 7 Hz, 1 H, C*H*Me), 3.60 (s, 3 H, NMe); ^{13}C NMR ($CDCl_3$) δ 210.2 (s), 89.8 (s), 57.1 (s), 47.8 (s), 40.8 (s), 38.8 (s), 36.0 (q), 35.5 (q), 34.2 (q), 30.8 (q), 29.8 (q), 28.3 (q), 27.9 (q), 23.6 (q). Anal. Calcd for $C_{14}H_{25}NS_2$: C, 61.96; H, 9.29; N, 5.16; S, 23.59. Found: C, 61.87; H, 9.46; N, 5.18; S, 23.41.

Irradiation of 14 in the Presence of 4a. Formation of Thietane 15. A solution of **14** and **4a** in benzene was irradiated for 3 h under similar conditions as described above. Workup of the reaction mixture gave **15** (68%) accompanied by the unchanged **14** (18%). The ^1H NMR spectrum of the recovered compound was identical with that of starting material **14**.

15: mp 86–88 °C; MS, m/z 283 (M^+), 209 ($M^+ - S{=}C(Me)_2$); ^1H NMR ($CDCl_3$) δ 1.05 (s, 3 H, Me), 1.25 (s, 3 H, NMe), 1.35 (s, 3 H, Me), 1.50 (s, 3 H, Me), 1.5–3.2 (m, 10 H), 3.45 (s, 3 H, NMe); ^{13}C NMR ($CDCl_3$) δ 206.1 (s), 86.4 (s), 57.2 (s), 51.0 (d), 47.6 (s), 40.0 (d), 36.2 (q), 30.4 (q), 26.4 (t), 25.8 (q), 23.5 (q), 23.0 (t), 20.1 (q), 19.8 (t), 18.1 (t). Anal. Calcd for $C_{15}H_{25}NS_2$: C, 63.58; H, 8.89; N, 4.97; S, 22.59. Found: C, 63.46; H, 8.79; N, 4.97; S, 22.68.

Irradiation of *N*-Alkyldithiophthalimides 16a–c in Benzene. A solution of **16** (5 mmol) in benzene (500 mL) was irradiated for 20 h. After workup of the reaction mixture, the unreacted dithiophthalimides **16a–c** were recovered quantitatively by column chromatography on silica gel.

Irradiation of *N*-Methyldithiophthalimide 17 in the Presence of 4a. A solution of **17** (5 mmol) and **4a** (25 mmol) in benzene (500 mL) was irradiated for 3 h. After removal of the solvent, the residue was chromatographed on silica gel to give thietane **18** and unsaturated thioamide **19** in 43% and 10% yields, respectively. Further, irradiation of the isolated **18** in benzene for 5 h gave quantitatively **19**.

18: mp 99–100 °C (hexane); MS, m/z 277 (M^+), 203 ($M^+ - S{=}C(Me)_2$); ^1H NMR ($CDCl_3$) δ 1.00 (s, 3 H, Me), 1.25 (s, 3 H, Me), 1.70 (s, 6 H, Me × 2), 3.80 (s, 3 H, NMe), 7.3–8.0 (m, 4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 194.1 (s), 145.1 (s), 137.2 (s), 130.6 (d), 128.9 (d), 125.1 (d), 124.7 (d), 81.2 (s), 57.0 (s), 47.4 (s), 35.7 (q), 29.7 (q), 29.0 (q), 26.8 (q), 23.6 (q). Anal. Calcd for $C_{15}H_{19}NS_2$: C, 64.94; H, 6.90; N, 5.05; S, 23.11. Found: C, 65.13; H, 6.86; N, 5.10; S, 23.37.

19: mp 161–162 °C (ethanol); MS, m/z 203 (M^+); ^1H NMR ($CDCl_3$) δ 2.40 (s, 6 H, Me × 2), 3.95 (s, 3 H, NMe), 7.2–8.2 (m, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 192.4 (s), 145.1 (s), 137.2 (s), 132.8 (s), 131.6 (s), 130.6 (d), 128.9 (d), 125.1 (d), 124.6 (d), 35.2 (q), 26.4 (q), 25.1 (q). Anal. Calcd for $C_{12}H_{13}NS$: C, 70.91; H, 6.45; N, 6.89; S, 15.75. Found: C, 70.88; H, 6.42; N, 6.95; S, 15.88.

Irradiation of 17 in the Presence of 2,5-Dimethyl-2,4-hexadiene (9). A solution of **17** (5 mmol) and **9** (25 mmol) in 500 mL of benzene was irradiated for 2 h and worked up as described above. Thietane **21** and unsaturated thioamide **22** were obtained in 42% and 18% yields, respectively. Each photoproduct was obtained as a 1:1 mixture of stereoisomers. Upon irradiation under the analogous conditions, the thietane **21** was easily converted to **22**.

21: MS, m/z 303 (M^+), 229 ($M^+ - S{=}C(Me)_2$); ^1H NMR ($CDCl_3$) δ 1.00, 1.30, 1.50, 1.65 (1:4:1:2 s, 3 H, Me × 4), 3.25, 3.30 (2 s, 3 H, NMe), 3.4–3.5 (2d, J = 8 Hz, 1 H, CHC=C), 5.1–5.5 (2 m, H, vinyl H), 7.2–7.8 (m, 4 H).

22: m/z 229 (M^+); ^1H NMR ($CDCl_3$) δ 1.40, 1.50, 1.75, 1.95 (4 s, 3 H, Me), 3.15, 3.25 (2 s, 3 H, NMe), 4.0–4.1 (2 d, J = 5 Hz, 1 H, vinyl H), 4.6–4.8 (2 m, 1 H, vinyl H), 7.2–7.7 (m, 4 H).

Irradiation of *N*-Methylmonothiosuccinimide 23 in the Presence of 4a. Formation of Thietane 24 and Oxetane 25. A solution of **23** (5 mmol) and **4a** (25 mmol) in benzene (500 mL) was irradiated for 6.5 h. The solvent was removed in vacuo, and the products were separated by column chromatography on silica gel, affording thietane **24** and oxetane **25** in 32% and 10% yields, respectively.

Thietane 24: mp 87–88 °C (hexane); MS, m/z 213 (M^+), 139 ($M^+ - S{=}C(Me)_2$); IR 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (s, 3 H, Me), 1.20 (s, 3 H, Me), 1.35 (s, 3 H, Me), 1.55 (s, 3 H, Me), 2.0–3.1 (m, 4 H), 3.05 (s, 3 H, NMe); ^{13}C NMR ($CDCl_3$) δ 175.0 (s), 75.8 (s), 57.4 (s), 46.6 (s), 35.9 (t), 30.3 (t), 30.1 (q), 27.1 (q), 26.6 (q), 24.0 (q), 22.7 (q). Anal. Calcd for $C_{11}H_{19}NOS$: C, 61.93; H, 8.98; N, 6.57; S, 15.03. Found: C, 62.03; H, 9.00; N, 6.33; S, 14.90.

Oxetane 25: colorless oil; MS, m/z 213 (M^+); ^1H NMR ($CDCl_3$) δ 1.10 (s, 3 H, Me), 1.20 (s, 3 H, Me), 1.30 (s, 3 H, Me), 1.50 (s, 3 H, Me), 2.0–3.1 (m, 4 H), 3.20 (s, 3 H, NMe); ^{13}C NMR ($CDCl_3$) δ 203.1 (s), 96.5 (s), 82.3 (s), 48.7 (s), 34.3 (t), 30.4 (t), 29.8 (t), 27.4 (q), 24.8 (q), 21.9 (q), 20.5 (q). Anal. Calcd for $C_{11}H_{19}NOS$: C, 61.93; H, 8.98; N, 6.57; S, 15.03. Found: C, 61.88; H, 9.04; N, 6.60; S, 15.11.

Irradiation of *N*-Methylmonothiophthalimide (26) in the Presence of 4a. Formation of Thietane 27. A solution of **26** (5 mmol) and **4a** (25 mmol) in benzene (500 mL) was irradiated for 1.5 h. Workup of the reaction mixture gave thietane **27** in 60% yield: mp 86.5–88.5 °C (hexane); MS, m/z 261 (M^+), 187 ($M^+ - S{=}C(Me)_2$); ^1H NMR ($CDCl_3$) δ 1.00 (s, 3 H, Me), 1.20 (s, 3 H, Me), 1.65 (s, 6 H, Me × 2), 3.40 (s, 3 H, NMe), 7.2–8.0 (m, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 164.8 (s), 144.2 (s), 137.9 (s), 130.9 (d), 129.0 (d), 126.8 (d), 124.9 (d), 81.5 (s), 57.2 (s), 47.4 (s), 35.9 (q), 29.3 (q), 28.8 (q), 26.2 (q), 24.6 (q). Anal. Calcd for $C_{15}H_{19}NOS$: C, 68.93; H, 7.83; N, 5.63; S, 12.27. Found: C, 68.95; H, 7.84; N, 5.47; S, 12.15.

Irradiation of *N*-Methylmonothiophthalimide (26) and *trans*-Stilbene (28). Formation of Thietanes 29a,b. A solution of **26** (5 mmol) and **28** (25 mmol) in 500 mL of benzene was irradiated for 1 h. The solvent was removed, and the products were separated by column chromatography on silica gel, affording two stereoisomers of thietanes **29a** and **29b** in 36% and 44% yields, respectively.

29a: mp 195–196 °C (ethanol); MS, m/z 235 ($M^+ - S{=}CHPh$); ^1H NMR ($CDCl_3$) δ 3.00 (s, 3 H, NMe), 5.35 (d, J = 10 Hz, 1 H, C*H*Ph), 5.50 (d, J = 10 Hz, 1 H, SC*H*Ph), 6.6–6.8 (m, 2 H, Ar H), 7.0–7.9 (m, 11 H, Ar H). Anal. Calcd for $C_{23}H_{19}NOS$: C, 77.28; H, 5.36; N, 3.92; S, 8.97. Found: C, 77.40; H, 5.38; N, 3.94; S, 8.94.

29b: mp 206–209 °C (ethanol); MS, m/z 235 ($M^+ - S{=}CHPh$); ^1H NMR ($CDCl_3$) δ 3.45 (s, 3 H, NMe), 5.15 (d, J = 10 Hz, 1 H, C*H*Ph), 5.45 (d, J = 10 Hz, 1 H, SC*H*Ph), 6.6–7.8 (m, 14 H, Ar H). Anal. Calcd for $C_{23}H_{19}NOS$: C, 77.28; H, 5.36; N, 3.92; S, 8.97. Found: C, 77.55; H, 5.31; N, 3.78; S, 8.88.

Irradiation of N-Asymmetrically Substituted Dithiosuccinimides 30 and 31. Photoracemization Test. A solution of **30** (5 mmol) in benzene (500 mL) was irradiated for 20 h. After removal of the solvent, the residue was chromatographed on silica gel column to give unchanged **30**. Recovered **30**, purified by distillation, was dissolved in benzene, and the 10 mM solution was used for measuring the optical activity in **30**. The resulting solutions, obtained from the repeated three runs, exhibited $[\alpha]^{20}_D$ values of −3.75°, −3.80°, and −3.78°. Under similar conditions, irradiations of **31** were carried out and repeated 3 times, and each optical rotation was measured with a Union PM-201 automatic polarimeter. The $[\alpha]^{20}_D$ values of recovered **31** in the three runs were −4.10°, −3.96°, and −4.02°.

Wavelength-Dependence Experiments for Formation of Thietane 5a. Irradiation at Various Wavelengths. A solution of **3** (5 mmol) and **4a** (25 mmol) in 100 mL of benzene was prepared. A 5-mL portion of this solution was placed into each of six Pyrex test tubes, which were then attached to a high-vacuum line, degassed with series of four freeze–pump–thaw cycles, and sealed. Each sample was irradiated at 250, 303, 356, 410, 463, and 510 nm for 2 h by a spectoirradiator. Yields for thietane **5a** formation at various wavelengths were determined by gas chromatographic analysis by using phenanthrene as an internal standard.

Quenching Experiments. Benzene solutions of **3** (50 mM) and **4a** (250 mM) containing varying amounts of ferrocene (50, 80, 100, 120, 150, and 200 mM) in Pyrex test tubes were degassed with a series of five freeze–pump–thaw cycles and sealed. The sample tubes were irradiated in parallel on a merry-go-round apparatus through a filter solution with two 1- and 5-cm compartments containing, separately, 9,10-dibromoanthracene (0.2 mg/mL) in toluene and crystal violet (0.025 mg/mL) in ethanol to isolate the 436-nm region.[17] Yields for thietane **5a** formation

(17) Cavert, J. G.; Pitt, J. N., Jr. "Photochemistry"; Wiley: New York, 1967; p 738.

were determined by gas chromatographic analysis as described above.

Quantum Yields. Benzene solutions of **3** (10 mM) and **4a** (50 mM) in four Pyrex test tubes were degassed with four freeze–pump–thaw cycles and sealed. Quantum yields were measured relative to 0.012 M potassium ferrioxalate actinometer with parallel irradiation of the samples under the same conditions. Yields for **5a** formation were determined by gas chromatographic analysis.

Sensitizing Experiments. Benzene solutions of **3** (50 mM) and **4a** (250 mM) containing varying amounts of triphenylene (50, 100, and 250 mM) in Pyrex test tubes were degassed with a series of five freeze–pump–thaw cycles and sealed. The sample tubes were irradiated by 500-W high-pressure mercury lamp in parallel on a merry-go-round apparatus. Yield for **5a** formation by addition of triphenylene was increased to 2.1 times in comparison with that in the absence of triphenylene.

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Registry No. **1a**, 89464-69-7; **1b**, 95765-51-8; **1c**, 90088-68-9; **1d**, 95765-52-9; **2a**, 95765-53-0; **2b**, 95765-54-1; **3**, 3889-18-7; **4a**, 563-79-1; **4b**, 513-35-9; **4c**, 115-11-7; **4d**, 590-18-1; **4e**, 109-92-2; **5a**, 95765-62-1; **5b**, 95765-63-2; **5c**, 95765-64-3; **5d**, 95765-65-4; **5e**, 95765-66-5; **7**, 95765-67-6; **9**, 764-13-6; *cis*-**10**, 95784-27-3; *trans*-**10**, 95797-80-1; (*E*)-**11**, 95765-68-7; (*Z*)-**11**, 95765-69-8; **12**, 95765-57-4; **13**, 95765-70-1; **14**, 95765-56-3; **15**, 95765-71-2; **16a**, 35373-06-9; **16b**, 35409-94-0; **16c**, 95765-55-2; **17**, 35373-10-5; **18**, 95765-72-3; **19**, 95765-73-4; *cis*-**21**, 95765-74-5; *trans*-**21**, 95765-75-6; (*E*)-**22**, 95765-76-7; (*Z*)-**22**, 95765-77-8; **23**, 2043-24-5; **24**, 95765-78-9; **25**, 95765-79-0; **26**, 14160-11-3; **27**, 92172-52-6; **28**, 103-30-0; **29a**, 95840-09-8; **29b**, 95840-10-1; **30**, 95765-80-3; **31**, 95765-81-4; ferrocene, 102-54-5; ethyl 2,3-dicyano-2,3,3-trimethylpropionate, 95765-58-5; ethyl 2-cyano-3,3-dimethylacrylate, 759-58-0; potassium cyanide, 151-50-8; methyl iodide, 74-88-4; 2,3,3-trimethylsuccinic acid, 2103-16-4; methylamine, 74-89-5; 1,3,3,4-tetramethylsuccinimide, 95765-59-6; (*S*)-(+)-1-bromo-2-methylbutane, 534-00-9; (*S*)-(+)-1-bromo-3-methylpentane, 22299-70-3; succinimide, 123-56-8; (*S*)-1-(2-methylbutyl)succinimide, 95765-60-9; (*S*)-1-(3-methylpentyl)succinimide, 95765-61-0; 1,3-cycloocatdiene, 1700-10-3; *N*-methylsuccinimide, 1121-07-9; *cis*-*N*-methylcyclohexane-1,2-dicarboximide, 64090-28-4; 1,2-cyclohexanedicarboxylic anhydride, 85-42-7; triphenylene, 217-59-4.

Total Synthesis of the Novel Coenzyme Methoxatin

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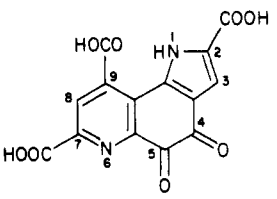
A convergent total synthesis of the novel coenzyme methoxatin (**1**) is described. This coenzyme is a pyrroloquinoline quinone tailored for efficient oxidation of methanol and formaldehyde in methylotrophic bacteria. The synthesis was achieved by joining pyrrole subunit **5a** with uvitonic acid ester **8b** followed by photocyclization of the resulting olefin **9** to deoxymethoxatin **10**. Conversion of **10** to methoxatin proceeded in five steps and led to some elaboration of the chemistry of the unusual pyrroloquinoline heterocycle. The overall yield is ~15% in 11 operations.

A number of bacteria, known as methylotrophs, can use methane or methanol as their sole source of energy and of carbon for synthesis. These organisms are currently of great interest as sources of single-cell protein for nutrition[2] and as a means of converting cheap raw materials such as methane and methanol into more complex structures. A crucial step in their metabolism is the conversion of methanol into formaldehyde and formic acid. The operative enzyme, methanol dehydrogenase[3] (EC 1.1.99.8), was found to be dependent on a coenzyme[4] not showing the usual spectroscopic characteristics of known redox coenzymes such as NADH/NADPH or flavins. Using ESR and ENDOR on the purified enzyme and on the isolated cofactor, Duine et al. established that the cofactor is a quinone containing two nitrogen atoms and three protons, one of which is exchangeable.[5] The actual structure (**1**) of the coenzyme was proposed by Forrest et al.[6] based upon



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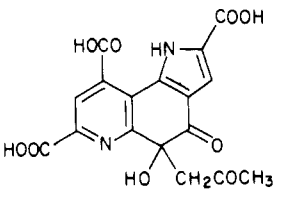

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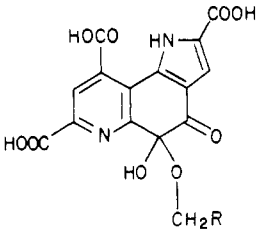

3

an X-ray study of its aldol adduct with acetone **2**, an artifact of the isolation. The structure was confirmed by ^{1}H NMR of the isolated cofactor and its trimethyl ester,[7] by four different total syntheses[8-11] (one of which[10] is our preliminary communication of this work), and by recon-

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