J. Org. Chem. 1994, 59, 2608–2612

Generation of Acyl Radicals from 2-Naphthyl Thioesters

John H. Penn* and Fang Liu

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

Received September 29, 1993[•]

A series of *S*-2-naphthyl thioesters were synthesized from the corresponding carboxylic acids or acid chlorides. Irradiation of these thioesters in the presence of a hydrogen source (i.e., 1,4-cyclohexadiene) generated the corresponding aldehydes. In this fashion, primary, secondary, tertiary, and aryl carboxylic acids were converted to the aldehydes in high yields. Intramolecular radical cyclization reactions support the hypothesis that the reaction proceeds via the formation of acyl radicals. The formation of aldehydes was not perturbed by possible Norrish Type II reactions.

Introduction

The generation of acyl radicals and their reaction with alkenes have been recognized as a useful and practical synthetic method for the formation of carbon–carbon bonds.[1] Traditionally, acyl radicals have been generated either thermally or photochemically. In the thermal generation of acyl radicals, an initiator (e.g., AIBN) is normally used to start a chain mechanism with Bu_3SnH and an acyl selenide[2] or an acyl chloride.[3] These generation techniques have the limitations expected from the higher temperatures required to initiate the reaction and from the radical chain mechanism which may be less tolerant of complex functionality when the methodology is applied to the synthesis of more complex molecules.

To overcome the disadvantage of high-temperature reaction conditions, photochemical methods have been developed involving sensitizers[4] or low-temperature initiators which abstract an aldehydic hydrogen (e.g., benzophenone, *tert*-butyl *p*-benzoylperbenzoate).[5] In general, the overall yields of these methods are not very high. More recent photochemical methods use acyl triphenyl germanium[6] compounds or acyl tellurides[7] as the immediate radical precursors. Due to the bulkiness of the triphenylgermyl group, steric problems prevented the intramolecular addition reaction in several internal alkenes. A limitation of the acyl telluride approach to acyl radicals resulted from the instability or lack of reactivity of the aliphatic acyl tellurides.[7] Therefore, significant limitations on the generation of acyl radicals make further efforts to develop new and generally useful alternatives worthwhile.

As part of our long-standing effort to be able to manipulate functional groups in substances as diverse as coal,[8,9] we embarked on a program of changing carboxylic acid functional groups to other functionality.[10] In line with this work, we reasoned that thioesters might be an excellent source of acyl radicals. We recognized that the photochemical generation of acyl radicals has the potential to yield these radicals at almost any desired temperature, in any solvent, and/or under any reaction conditions. We also desired a photochemical method that would be applicable despite the presence of any other functionality in a molecule and would be insensitive to the type of photochemical equipment. We chose the *S*-2-naphthyl thioesters for the following reasons: (1) absorption of light by these molecules should be at longer wavelengths than the light absorption by most normal organic compounds in order to minimize light absorption and possible photochemical reactions in other parts of the molecule; (2) the anticipated product of the reaction (i.e., 2-naphthalenethiol) would absorb light but not undergo significant competing reactions; (3) the *S*-2-naphthyl thioester should have a π–π^* excited state, minimizing possible competing reactions from Norrish Type II reactions; (4) 2-naphthalenethiol is readily available, making the syntheses of the thioesters facile; and (5) preliminary reports[11,12] on the photochemical reactions of thioesters suggested that C–S bond cleavage was likely to be the major reaction pathway. The compounds chosen for this study are depicted in Scheme 1 and were chosen to represent a wide variety of possible functionality which might be encountered in any attempt to utilize this methodology in general practice. The results of irradiation of these thioesters in order to form acyl radicals is reported here.

Results and Discussion

Thioester Synthesis. Thioesters for this study were readily obtained using standard methodology.[11,13–15] When the acid chloride was commercially available, the desired thioesters were readily obtained in high yields by refluxing the acid chloride and 2-naphthalenethiol in a pyridine-containing benzene solution.[13] For those compounds with

---

[•] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

(1) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429.

(2) Kerr, J. A.; Lioyd, A. C. *Trans. Faraday Soc.* **1967**, *63*, 2480.

(3) Cekovicm Z. *Tetrahedron Lett.* **1972**, 749.

(4) Fraser-Reid, B.; Anderson, R. C.; Hicks, D. R.; Walker, D. L. *Can. J. Chem.* **1977**, *55*, 3986.

(5) Gottschalk, P.; Neckers, D. C. *J. Org. Chem.* **1985**, *50*, 3498.

(6) Kiyooka, S.; Kaneko, Y.; Matsue, H.; Hamada, M.; Fujiyama, R. *J. Org. Chem.* **1990**, *55*, 5562.

(7) Chen, C.; Crich, D.; Papadatos, A. *J. Am. Chem. Soc.* **1992**, *114*, 8313.

(8) (a) Penn, J. H.; Owens, W. H. *J. Am. Chem. Soc.* **1993**, *115*, 82. (b) Penn, J. H.; Owens, W. H.; Peterson, J. L.; Finklea, H. O.; Snider, D. A. *J. Org. Chem.* **1993**, *58*, 2128.

(9) Penn, J. H.; Owens, W. H. *Tetrahedron Lett.* **1992**, *33*, 3737.

(10) A previous report from these labs[9] suggested that acyl anions could be formed from reduction of thioesters with alkali metals. This report appears to be in error. Attempts to reproduce the aldehyde formation from *S*-phenyl benzenecarbothioate (i.e., quenching with methanol) resulted in minor amounts of the aldehyde, but produced benzoin as the major product. Quenching with methyl iodide produced the methyl ether of benzoin. These results suggest that the intermolecular reactions of the acyl anions and/or acyl radicals generated from the radical anion of the thioester are more important than we originally suspected.

(11) Tomioka, H.; Takimoto, Y.; Kawabata, M.; Harada, M.; Fouassier, J. P.; Ruhlmann, D. *J. Photochem. Photobiol.* A **1990**, *53*, 359.

(12) Gaber, A. E. M. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1991**, 55, 211.

(13) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. Vogel's. *Textbook of Practical Organic Chemistry*, 4th ed.; 1978 p 1139.

(14) Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques, A Microscale Approach*; 1990, p 368.

(15) Wissner, A.; Grudzinskas, C. V. *J. Org. Chem.* **1978**, *43*, (20), 3973.

0022-3263/94/1959-2608$04.50/0

Scheme 1. Compounds Chosen for Study

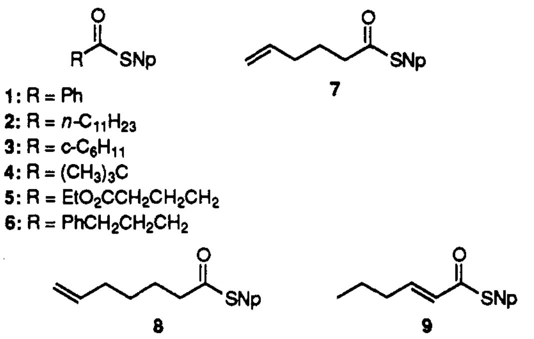


Table 1. Photochemical Reactions of Thioesters

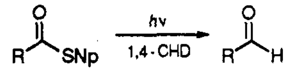
compound	wavelength (nm)	time (h)	conversion (%)	product yields (mol %) RCHO	product yields (mol %) 2,4-DNP Derivative
1	254	100	100	90	-
	300	160	100	78	-
2	254	110	100	97	85
	sunlamp	110	91	74	-
3	254	116	81	99	101
	300	43	96	84	-
	sunlamp	110	88	71	-
4	254	116	86	-	74
5	sunlamp	110	100	99	86
6	300	43	97	74	-
	sunlamp	98	81	-	89

more sensitive functionality and for which the acid chloride was not available commercially, oxalyl chloride was used to generate the acyl chloride[14] which was treated in situ with 2-naphthalenethiol to afford the thioester with good to excellent yields. Alternatively, the carboxylic acid could be treated with thionyl chloride and converted to the thioester in an analogous fashion.[15] See the Experimental Section for full details of the syntheses.

Photochemical Reactions of Thioesters. Irradiation of these thioesters was performed in benzene solution to minimize possible complications from competing radical reactions. 1,4-Cyclohexadiene (CHD, 0.4 mM) was added as a sacrificial hydrogen source to provide termination of the radical chain reactions. Data relevant to important details of the experimental reaction conditions, the fate of the carbonyl portion of the molecule, and yield data are gathered in Table 1. The corresponding aldehydes were first identified as reaction products by their identical retention times and identical mass spectra, as compared to authentic samples. The structural assignments were confirmed by isolation of the 2,4-dinitrophenylhydrazone derivatives (2,4-DNP derivatives) and comparison of their melting points, spectra (^{1}H NMR, ^{13}C NMR and/or GC-MS spectra), and other physical properties with previously reported literature data. The sulfur-containing part of the molecule was less well characterized but appears to have been converted to both 2-naphthalenethiol and 2-naphthyl disulfide. The relative amounts of these products varied with the reaction conditions and irradiation time. Since this product was not of interest, its characterization was not pursued further.

The yields of the reactions were determined through GC analysis and/or by isolation of their 2,4-DNP derivatives. GC yield data were obtained by using *n*-hexadecane as an internal standard and the determination of appropriate instrumental response functions. GC yield data were unavailable in the case of the *tert*-butyl thioester 4, where the aldehyde did not separate sufficiently from solvent to allow a satisfactory analysis and in the case of 4-phenylbutyl thioester 6 where no authentic aldehyde was available for the determination of response factor and appropriate calibration data. The yield data were confirmed by isolation of the 2,4-DNP derivatives. Isolated yield data for 2,4-DNP derivatives were collected for all compounds in this study, except for *S*-naphthyl benzenecarbothioate which has been previously studied by Gaber.[12] These data are gathered in Table 1 and show that >85% isolated yield was obtained in all cases. The single exception to these excellent yields was that of *tert*-butyl 4 where only 74% of the 2,4-DNP derivative was isolated. We attribute the lower yield of this reaction to the competition from the fast decarbonylation of the tertiary radical.[1] Alternatively, the steric effects of the *tert*-butyl group may slow down the hydrogen abstraction from the cyclohexadiene. No further effort was made to understand the origin of the diminished yields since all other yields were excellent.

These results are rather remarkable. In this series, aryl, primary, secondary, and tertiary *S*-naphthyl thioesters lead cleanly to high yields of the corresponding aldehydes. The substrates seem not to be sensitive to the light source, since sunlamp, 300-nm, and 254-nm irradiations give similar yields. This is in line with the goal of this research on which the naphthyl group was used to capture the light and initiate the photochemistry. Since the 2-naphthylthio group is of little concern, the absorption of light by the products (and hence secondary photochemistry) is minimized. The reaction is thus represented by eq 1.



(1)

Perhaps more remarkable are the results of the 4-phenylbutyl thioester 6 and the 4-(ethoxycarbonyl)butyl thioester 5. The Norrish Type II hydrogen atom abstraction reaction is such a general and ubiquitous reaction that it is a nuisance at best and will totally dominate the chemistry of most carbonyl groups. The choice of 5 and 6 was designed to investigate the possible competition of the intramolecular Norrish Type II reaction. These compounds would be ideal candidates for this reaction because of the stabilization of the incipient radical center by either the phenyl group or the ethoxycarbonyl group. In contrast to the reaction of 4-phenylbutanoate where the Norrish Type II reaction is the major reaction pathway and proceeds with a quantum yield of 0.5,[16] the reaction of *S*-naphthyl 4-phenylbutanethiolate proceeds to give the corresponding aldehyde as expected in this study. Ester 5 is also expected to have a strong competition from the intramolecular Norrish Type II reaction but goes cleanly to the aldehyde as shown in Table 1.

The radical nature of the reaction was probed via the use of alkenoyl cyclization reactions. The results of irradiation of *S*-naphthalen-2-yl 5-hexenethioate (7) and *S*-naphthalen-2-yl 6-heptenethioate (8) are presented in eqs 2 and 3 and in Tables 2 and 3. The product yields presented here are those obtained from GC analyses as described above.

The results for 5-hexenyl 7 are particularly instructive. Under all conditions, 2-methylcyclopentanone (11) is formed as the major product of the reaction, with only a

---

[16] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 169.

Table 2. Irradiation of 7

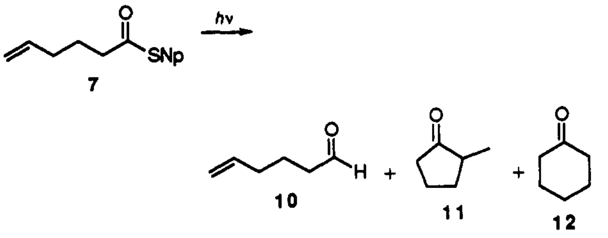
reaction conditions	time (h)	conversion (%)	product distribution (%) 10	11	12
sunlamp, 65 °C	97[a]	100	20	74	6
	97	100	3	78	19
sunlamp, 54 °C	25	17	3	83	14
	48	68	6	80	14
	65	97	7	81	13
	71	100	6	81	13
	98	100	6	81	13
	116	100	6	81	13
350 nm, 28 °C	65	68	11	81	8
	99	80	12	80	8

[a] 1 mol equiv 1,4-cyclohexadiene (CHD) added.

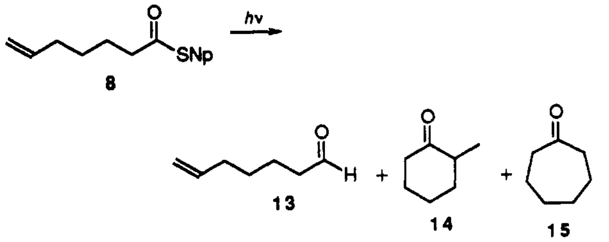
Table 3. Irradiation of 8

reaction conditions	time (h)	conversion (%)	product distribution (%) 13	14	15
sunlamp, 65 °C	97[a]	100	79	16	5
	97	100	50	26	24
sunlamp, 54 °C	25	25	66	19	15
	48	63	65	21	14
	65	76	66	21	13
	71	85	66	21	13
	98	100	63	22	15
	116	100	67	21	12
350 nm, 28 °C	65	28	79	14	7
	99	57	78	15	7

[a] 2.8 mol equiv of 1,4-cyclohexadiene (CHD) added.



(2)



(3)

small amount of cyclohexanone (12) or the corresponding aldehyde 10 being observed in the reaction. The product ratio is not affected by the extent of conversion, indicating that no secondary photochemistry is occurring in these reactions. The relative product ratios also are not affected by the length of irradiation time, also indicating no secondary photolysis. In contrast, the product ratios are influenced by the amount of 1,4-cycloohexadiene (CHD) added to the reaction solution. When a 1:1 molar ratio of CHD to the thioester is used, then a large proportion of acyl radicals are trapped and form 10, as opposed to ring formation to form 12. The slightly diminished yield of 11 also indicates that trapping of the acyl radical competes with the cyclization reaction. Thus, the straight-chain aldehyde is formed in significantly greater amounts than is formed in those experiments containing no added CHD. A slight trend in the amount of straight chain product to the amount of 11 and 12 is seen in the temperature dependence of the reaction. Lower temperatures seem to form more straight-chain products. If this is true, then cyclization to form 11 or 12 could be an activated process.

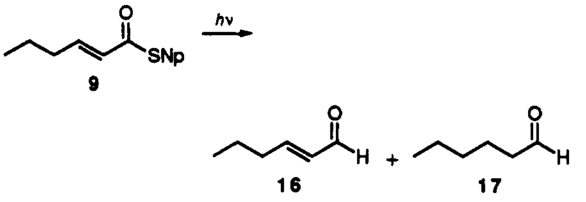
Table 4. Quantum Yield Determinations

compound	quantum yield (ϕ)
3	0.01
6	0.008

However, the experimental error in the data presented here make a conclusive interpretation difficult.

In contrast to the reactions of 7, 6-heptenyl 8 produced the corresponding aldehyde 13 as the major product. The large amount of 13 formed in this reaction is consistent with the radical character of the reaction, paralleling the relatively slow cyclizations of the 6-heptenoyl radical to form 2-methylcyclohexanones or heptanones.

A final effort to explore the generality of the reaction was made by examining the reactions of α,β-unsaturated thioesters. Irradiation of *S*-2-naphthyl *trans*-2-hexenethioate (9) proved to be a sensitive function of added CHD. With 2.2 molar equiv of added CHD, the reaction proceeded exclusively to yield hexanal (17). With less added hydrogen donor (i.e., 1.5 molar equiv), the reaction proceeded to give ca. an 85:15 ratio of hexanal to *trans*-2-hexenal. Even when no CHD was added, ca. 12% of hexanal was formed (relative to 88% of *trans*-2-hexenal) (eq 4). This indicates that reduction of the alkene is a powerful driving force and may ultimately prevent the use of thioester methodology in α,β-unsaturated acid reductions.



(4)

Quantum Yield Determinations. Since all reactions proceeded with nearly identical efficiencies, we have measured the quantum yields (ϕ) of the photoreactions of 3 and 6. As can be seen in Table 4, the quantum yields for these reactions are small, being of the order of 0.01. Although these quantum yields are small, this is not a serious deterrent to their general usage in synthetic methodology, since it has been shown that there are relatively few complications from secondary photolysis of the products. Additionally, equipment is available to concentrate light to do reactions in a reasonable length of time.

Summary

The use of 2-naphthyl thioesters appears to be a promising method for the photochemical production of acyl radicals under mild conditions. Addition of 1,4-cyclohexadiene serves to provide a hydrogen source which yields aldehydes from aryl, primary, secondary, and tertiary thioesters when irradiated with almost any light source. Cyclization reactions suggest the intermediacy of acyl radicals in the reaction. Work is currently in progress in these laboratories to further explore the generality of this reaction.

Experimental Section

Melting points were determined on a Laboratory Devices Mel-Temp apparatus and were uncorrected. Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model

5890A GLC equipped with a 10-m 5% phenylmethylsilicone column. Integration of the signals was performed by a Hewlett-Packard Model 3390A digital integrator. GC-MS were measured with a Hewlett-Packard Model 5980 GC-MS using a 25-m HP-1 (cross-linked methyl silicone) column for the analytical separations and molecular mass (M^+) determinations at an ionization potential of 70 eV. FTIR spectra were recorded either neat on sodium chloride plates or in the indicated solution on a Perkin-Elmer Model 1600 IR spectrophotometer. Data are reported in wavenumbers (cm^{-1}). ^{1}H NMR (270 MHz) and ^{13}C NMR (67.9 MHz) spectra were measured with $CDCl_3$ as the solvent and TMS (^{1}H δ 0.0 ppm), $CHCl_3$ (^{1}H δ 7.26 ppm), or $CDCl_3$ (^{13}C δ 77.0 ppm) as internal standards on a JEOL GX-270 NMR spectrometer (chemical shifts δ (ppm) and coupling constants J (Hz)). UV-vis spectra were measured with a Hewlett-Packard Model 8452A Diode Array spectrometer in hexane solution.

All dark reactions were monitored by thin-layer chromatography (TLC). TLC was carried out on 0.25-mm E. Merck silica gel plates (60F-254), and visualization was effected with short-wavelength UV light or 10% ethanolic phosphomolybdic acid with heat. Preparative thin-layer chromatography (prep TLC) was performed on Analtech Uniplates 0.5 mm (or 1.0 mm) × 20 cm × 20 cm glass-supported silica gel plates (60F-254). EM Science silica gel 60 (70–230 mesh ASTM) was used for flash column chromatography.

Benzene was distilled from sodium benzophenone ketyl under argon prior to use. Pyridine was dried over potassium alkoxide (KOH). Unless noted otherwise, chemicals were purchased from Aldrich Chemical Co. and used directly.

Thioester Synthesis. Three general methods for the syntheses of the thioesters were used.

Method A. Into a solution of the acid chloride (3.0 mmol) in benzene (2.0 mL) in a dry round-bottomed flask equipped with a stirring bar, a condenser, and a driving tube was added 2-naphthalenethiol (320 mg, 2.0 mmol) in benzene (1.0 mL), followed by pyridine (2 drops). The solution was refluxed at 90 °C for 30 min. After cooling to ambient temperature, the mixture was poured into benzene, extracted (aqueous $NaHCO_3$), and dried over anhyd Na_2SO_4. Following solvent removal in vacuo, the residue was purified by gradient chromatography (hexane/diethyl ether) to afford the desired 2-naphthyl thioester.

Method B. Thionyl chloride (1.4 mmol) was added slowly to a solution of the carboxylic acid (1.5 mmol) in benzene solution (1.0 mL) in a flask equipped with a stirring bar, a condenser, and a drying tube. After reflux of the above solution at 90 °C for 4 h, a solution of 2-naphthalenethiol (0.9 mmol) in benzene (2.0 mL) was added, followed by pyridine (1.0 mL). After stirring for 30 min, the mixture was poured into benzene and worked up using the same procedure as described in method A.

Method C. In a dry round-bottomed flask equipped with a magnetic stirring bar was dissolved the carboxylic acid (2.0 mmol) in benzene (1.5 mL) under argon. To this solution at 0 °C was added oxalyl chloride followed by dimethylformamide (0.1 mL) dropwise. After the reaction mixture was stirred at rt (30 min), a solution of 2-naphthalenethiol (2.0 mmol) in benzene (1.0 mL) was added, followed by pyridine (0.5 mL). The resulting yellowish solution was stirred at rt (30 min) and then worked up according to the procedure described in Method A.

***S*-Naphthalen-2-yl Benzenecarbothioate (1)**: method A; 98% yield; colorless crystals; mp 108–9 °C (lit.[12] 108 °C); ^{1}H NMR δ 8.1 (3H, m), 7.8 (3H, m), 7.4 (6H, m) ppm; ^{13}C NMR δ 190.1, 136.6, 135.0, 134.9, 133.7, 133.4, 131.4, 128.8, 128.0, 127.8, 127.6, 127.5, 127.2, 126.5, 124.7 ppm; FTIR (CCl_4) 3050, 3030, 1682, 1580, 1503, 1445, 1203, 1174 cm^{-1}; UV-vis λ_{max} (ϵ) 304 (3900), 300 (4600), 292 (6900), 272 (11000) nm; GC-MS *m/e* (relative intensity) 264 (M, 1.4), 159 (2), 105 (100), 77 (51), 51 (20).

***S*-Naphthalen-2-yl Undecanethioate (2)**: method B; 99% yield; colorless crystals; mp 35–6 °C; ^{1}H NMR δ 7.9 (1H, s), 7.8 (3H, m), 7.4 (3H, m), 2.6 (2H, t, J = 9.0 Hz, CH_2CH_2CO), 1.6 (2H, apparent t, J = 7.7 Hz, $CH_2CH_2CH_2CO$), 1.4 (14H, m), 0.7 (3H, t, J = 7.7 Hz, CH_3CH_2) ppm; ^{13}C NMR δ 197.6, 134.2, 133.5, 133.2, 130.9, 128.6, 127.9, 127.7, 127.0, 126.4, 125.3, 43.7, 31.8, 29.5, 29.4, 29.3, 29.2, 28.9, 25.6, 22.6, 14.1 ppm; FTIR (CCl_4) 3058, 2927, 2855, 1711, 1558, 1501, 1465, 1132, 944 cm^{-1}; UV-vis λ_{max} (ϵ) 300 (2100), 290 (6900), 282 (7000), 262 (9000) nm; GC-MS *m/e* (relative intensity) 328 (M, <1), 169 (5), 160 (51), 128 (7), 127 (3), 115 (30), 113 (1), 99 (2), 85 (18), 71 (25), 57 (65), 55 (52), 43 (100), 41 (61).

***S*-Naphthalen-2-yl Cyclohexanecarbothioate (3)**: method B; 100% yield; colorless crystals; mp 59–60 °C; ^{1}H NMR δ 7.9 (1H, s), 7.8 (3H, m), 7.4 (3H, m), 2.6 (1H, m), 2.0 (2H, m), 1.8 (2H, m), 1.6 (3H, m), 1.3 (3H, m) ppm; ^{13}C NMR δ 200.8, 134.2, 133.5, 133.2, 131.0, 128.5, 127.8, 127.7, 126.9, 126.4, 125.2, 52.5, 29.5, 25.5, 25.4 ppm; FTIR (CCl_4): 3057, 2934, 2856, 1706, 1587, 1501, 1450, 1140, 964 cm^{-1}; UV-vis λ_{max} (ϵ) 300 (2400), 296 (3800), 280 (6200), 230 (40000) nm; GC-MS *m/e* (relative intensity) 271 (MH^{+1}, <1), 270 (M, 4), 160 (31), 128 (6), 115 (28), 83 (100), 55 (51).

***S*-Naphthalen-2-yl 2,2-Dimethylpropanethioate (4)**: method A; 84% yield; colorless crystals; mp 77–8 °C; ^{1}H NMR δ 7.9 (1H, s), 7.8 (3H, m), 7.4 (3H, m), 1.3 (9H, s, $(CH_3)_3C$) ppm; ^{13}C NMR δ 204.7, 134.7, 133.5, 133.2, 131.4, 128.6, 127.8, 127.7, 126.9, 126.4, 125.4, 47.0, 27.4 ppm; FTIR (CCl_4) 3061, 2964, 2867, 1696, 1558, 1500, 1476, 1365, 928 cm^{-1}; UV-vis λ_{max} (ϵ) 300 (2200), 296 (4000), 290 (5400), 274 (7300), 260 (10000) nm; GC-MS *m/e* (relative intensity) 244 (M, 6), 160 (30), 115 (26), 85 (15), 57 (100).

5-[(Naphthalen-2-ylthio)carbonyl]pentanecarboxylic Acid, Ethyl Ester (5): method A; 98% yield; colorless crystals; mp 33–4 °C; ^{1}H NMR δ 7.9 (1H, s), 7.8 (3H, m), 7.4 (3H, m), 4.1 (2H, q, J = 6.9 Hz, CH_3CH_2O), 2.8 (2H, t, J = 6.9 Hz, CH_2CH_2-COO), 2.4 (2H, t, J = 6.9 Hz, CH_2CH_2COS), 2.0 (2H, quintet, J = 7.8 Hz), 1.2 (3H, t, J = 6.9 Hz, CH_3CH_2) ppm; ^{13}C NMR δ 196.9, 172.6, 134.2, 133.4, 133.2, 130.8, 128.7, 127.9, 127.7, 127.1, 126.5, 124.9, 60.4, 60.3, 33.0, 20.6, 14.1 ppm; FTIR (CCl_4) 3057, 2982, 2933, 1736, 1709, 1558, 1501, 1375, 1158, 945 cm^{-1}; UV-vis λ_{max} (ϵ) 300 (2300), 292 (4800), 282 (6400), 272 (6500), 260 (8700) nm; GC-MS *m/e* (relative intensity) 257 (3), 160 (16), 143 (64), 115 (100), 87 (71), 55 (53), 43 (45).

***S*-Naphthalen-2-yl 4-Phenylbutanethioate (6)**: method C; 92% yield; yellow crystals; mp 47–8 °C; ^{1}H NMR δ 7.9 (1H, s), 7.8 (3H, m), 7.4 (3H, m), 7.2 (5H, m), 2.6 (4H, apparent t, J = 8.0 Hz, $PhCH_2CH_2$ and CH_2CH_2COS), 2.0 (2H, m, $CH_2CH_2CH_2$) ppm; ^{13}C NMR δ 197.4, 141.0, 134.2, 133.5, 133.2, 130.9, 128.7, 128.5, 128.4, 127.9, 127.7, 127.0, 126.5, 126.0, 125.1, 43.1, 35.2, 27.7 ppm; FTIR (CCl_4) 3085, 3059, 3028, 2935, 1709, 1586, 1498, 1454, 1345, 1059, 944 cm^{-1}; UV-vis λ_{max} (ϵ) 300 (2000), 296 (3400), 272 (6400), 260 (9200) nm; GC-MS *m/e* (relative intensity) 160 (31), 147 (40), 129 (9), 119 (2), 115 (36), 105 (5), 91 (100), 77 (10), 65 (19), 55 (37), 44 (30).

***S*-Naphthalen-2-yl 5-Hexenethioate (7)**: method C; 100% yield; yellowish oil; ^{1}H NMR δ 7.9 (1H, s), 7.7 (3H, m), 7.4 (3H, m), 5.7 (1H, m, $CH_2{=}CHCH_2$), 5.0 (2H, m, $CH_2{=}CH$), 2.6 (2H, t, J = 7.2 Hz, CH_2CH_2COS), 2.0 (2H, m, $CH_2CH_2CH{=}$), 1.7 (2H, m, $CH_2CH_2CH_2$) ppm; ^{13}C NMR δ 197.6, 137.4, 134.3, 133.5, 133.3, 130.9, 128.8, 128.0, 127.8, 127.1, 126.5, 125.2, 115.7, 42.9, 32.8, 24.6 ppm; FTIR (neat) 3083, 3056, 2968, 2930, 2861, 1706, 1640, 1586, 1500, 1453, 1414, 1344, 1268, 1132, 1058, 995, 916, 856, 813, 744 cm^{-1}; UV-vis λ_{max} (ϵ) 300 (3000), 296 (4800), 280 (8100), 264 (9300), 260 (11000) nm; GC-MS *m/e* (relative intensity) 256 (M, 3), 160 (40), 128 (4), 115 (35), 97 (12), 69 (53), 55 (37), 41 (100).

***S*-Naphthalen-2-yl 6-Heptenethioate (8)**: method C; 72% yield; yellowish oil; ^{1}H NMR δ 7.9 (1H, s), 7.7 (3H, m), 7.4 (3H, m), 5.7 (1H, m, $CH_2{=}CHCH_2$), 4.9 (2H, m, $CH_2{=}CH$), 2.6 (2H, t, J = 8.8 Hz, CH_2CH_2COS), 2.0 (2H, m, $CH_2CH_2CH{=}$), 1.7 (2H, m, $CH_2CH_2CH_2$), 1.4 (2H, m, $CH_2CH_2CH_2$) ppm; ^{13}C NMR: δ 197.3, 138.1, 134.1, 133.4, 133.2, 130.8, 128.6, 127.8, 127.6, 126.9, 126.4, 125.1, 114.8, 43.4, 33.2, 28.0, 24.9 ppm; FTIR (neat) 3062, 3056, 3000, 2930, 2859, 1702, 1640, 1586, 1500, 1458, 1413, 1344, 1268, 1132, 943, 911, 857, 813, 744, 680 cm^{-1}; UV-vis λ_{max} (ϵ) 300 (2000), 296 (3900), 272 (7700), 246 (24000) nm; GC-MS *m/e* (relative intensity) 270 (M, 4), 160 (50), 128 (4), 115 (32), 111 (7), 83 (19), 55 (100), 44 (52), 41 (57).

***S*-Naphthalen-2-yl *trans*-2-Hexenethioate (9)**: method C; 78% yield; yellowish oil; ^{1}H NMR δ 7.9 (1H, s), 7.8 (3H, m), 7.5 (3H, m), 7.0 (1H, dt, J = 15.4, 7.0 Hz, $CH_2CH{=}CHCOS$), 6.2 (1H, dt, J = 15.7, 1.4 Hz, $CH_2CH{=}CHCOS$), 2.2 (2H, dt, J = 7.0, 1.4 Hz, $CH_2CH_2CH{=}$), 1.5 (2H, m, $CH_3CH_2CH_2$), 0.9 (3H, t, J = 7.4 Hz, CH_3CH_2) ppm; ^{13}C NMR δ 188.0, 146.7, 134.3, 133.4, 133.2, 131.0, 128.6, 127.8, 127.7, 126.9, 126.4, 125.0, 34.2, 21.1, 13.6 ppm; FTIR (neat) 3057, 2963, 2932, 2869, 1686, 1634, 1583, 1558, 1501, 1457, 1157, 1023, 970, 890, 856 cm^{-1}; UV-vis λ_{max} (ϵ) 300 (5700), 290 (8800), 272 (12000) nm; GC-MS *m/e* (relative intensity) 256 (M, 2), 160 (6), 115 (24), 97 (72), 69 (7), 55 (100), 41 (28).

Photochemical Reactions of Thioesters. General Procedure. In a typical photochemical reaction, 1,4-cyclohexadiene (0.4 mmol, if necessary), hexadecane (40.0 μL, as an internal standard), and the thioester (0.2 mmol) in dry benzene (1.0 mL) were placed in a Pyrex tube. The solution was degassed with two freeze-pump-thaw cycles and sealed under vacuum. The solution was then irradiated at the indicated wavelength with either a merry-go-round reactor or a sunlamp for the indicated length of time. Quantitative analysis of the reaction was performed either by GC (or GC-MS) or separation by flash chromatography.

Alternatively, 2.0 mL of benzene was added to the reaction solution. The (2,4-dinitrophenyl)hydrazine solution (0.10 M, 1.2 equiv) made by the procedure described in ref 14 was added slowly with stirring. The solution was neutralized with saturated aqueous sodium bicarbonate (1.0 mL), washed with saturated aqueous sodium chloride (2 × 3 mL), and dried over anhydrous sodium sulfate. After removal of solvent in *vacuo*, the resulting residue was purified by flash chromatography to give the corresponding 2,4-dinitrophenylhydrazone derivative. Yield data are gathered in Table 1. The mp of the 2,4-DNP derivatives are given below with their corresponding literature values.

Undecanal 2,4-Dinitrophenylhydrazone: mp 104–5 °C (lit.[17] 104 °C).

Cyclohexanecarbaldehyde 2,4-Dinitrophenylhydrazone: mp 170–1 °C (lit.[18] 172 °C).

Pivalaldehyde 2,4-Dinitrophenylhydrazone: m.p. 208–9 °C (lit.[19] 208–209 °C).

4-Carbethoxybutanal 2,4-Dinitrophenylhydrazone: mp 66–7 °C (lit.[20] 66.5 °C).[21]

4-Phenylbutanal 2,4-Dinitrophenylhydrazone: mp 97–8 °C (lit.[22] 95–7 °C).

5-Hexenal 2,4-Dinitrophenylhydrazone: mp 95–6 °C (lit.[23] 96 °C).

6-Heptenal 2,4-Dinitrophenylhydrazone: mp 93–4 °C (lit.[24] 95 °C).

(*E*)-2-Hexenal 2,4-Dinitrophenylhydrazone: mp 104–5 °C (lit.[25] 104 °C).

Quantum Yield Determinations. A solution of the appropriate thioester and hexadecane in 1,4-cyclohexadiene containing benzene, and a solution of valerophenone (0.100 M) as an actinometer (ϕ = 0.33)[26] and hexadecane in benzene, were prepared to be exactly the same in optical density and were irradiated simultaneously at 300 nm in a merry-go-round apparatus. The quantum yield of disappearance was determined by measuring the amount of thioester relative to an internal standard.

Acknowledgment. We acknowledge the assistance of Ms. Ji-hong Yu in the final preparation of this manuscript.

Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra of **2**–**10** (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(17) Huntress, E. H.; Mulliken, S. P. *Identification of Pure Organic Compounds*; Wiley: New York, 1941.

(18) Heilbren, I.; Jones, E. R. H.; Richardsin, R. W. R.; Sondheimer, F. *J. Chem. Soc.* **1949**, 733.

(19) Rabjohn, N.; Schwarz, R. M. *J. Org. Chem.* **1983**, *48*, 1931.

(20) Cuvigny, T. *Ann. Chim.* **1956**, *13* (1), 475.

(21) Note added in proof: Glutaraldehydic acid, ethyl ester, has been previously reported, but incompletely characterized. The following spectral data are offered to prove its structure: ^{1}H NMR δ 9.8 (1H, t, J = 1.3 Hz, CHO), 4.1 (2H, q, J = 7.1 Hz, CH_3CH_2O), 2.5 (2H, td, J = 7.2, 1.3 Hz, CH_2CH_2CHO), 2.4 (2H, t, J = 7.3 Hz, $OOCCH_2CH_2$), 1.9 (2H, m, $CH_2CH_2CH_2$), 1.3 (3H, t, J = 7.1 Hz, CH_3CH_2O) ppm; ^{13}C NMR δ 159.8, 145.4, 130.0, 128.3, 123.6, 123.4, 116.6, 35.6, 27.3 ppm; FTIR (neat) 2981, 2938, 2825, 2725, 1732, 1448, 1376, 1247, 1164, 1030 cm^{-1}; GC-MS *m/e* (relative intensity) 116 (5), 99 (36), 98 (27), 88 (41), 85 (6), 71 (48), 70 (39), 60 (55), 42 (100).

(22) Meyers, A. I.; Munavu, R.; Durandetta, J. *Tetrahedron Lett.* **1972**, *37*, 3929.

(23) Burford, R. R.; Hewgill, F. R.; Jeffries, P. R. *J. Org. Chem.* **1962**, *27*, 4662.

(24) Lebel, N. A.; Post, M. E.; Whang, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 3759.

(25) Rapport, Z. *Handbook of Tables for Organic Compound Identification*, 3rd ed.; 1967.

(26) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896.