^{13}C NMR spectroscopy. The data indicate that for the protonated acid the hydrate form is strongly predominant, with very little free carbonyl to be observed in the equilibrium. For the dianion, however, the carbonyl form is present to ca. 10% at 20 °C, its proportion increasing linearly with temperature. This behavior resembles that observed in carbohydrates (cf. ref 27).

The data shown in Figures 1 and 2 suggest an attempt to estimate the lower limit for the rate constant of $O_2^{\bullet-}$ addition; if this reaction is considered to be the rate-limiting step of the propagating sequence, its rate constant $k_{addition}$ can be extracted. In the steady-state approximation from $v_{initiation} = v_{termination}$ we obtain $[O_2^{\bullet-}]_{steady\ state}$. Moreover, $v_{propagation} = k_{addition}[O_2^{\bullet-}]_{steady\ state}[\text{-CO-}]$, where -CO- signifies ketomalonate carbonyl form.

The present situation is described by equation 17 (r, dose rate). There are two sets of experiments which allow the calculation of $k_{addition}$: the dose rate dependence in Figure 1 and the ketomalonate dependence shown in the inset of Figure 2. The former data set yields $k_{addition}$ = 120 dm^3 mol^{-1} s^{-1}, and from the latter $k_{addition}$ = 150 dm^3 mol^{-1} s^{-1} is calculated. Considering that two independent data sets are used the agreement is quite satisfactory.

$$G(\text{peroxalate}) = \{G(O_2^{\bullet-})\}^{1/2}\left(\frac{k_{addition}}{(k_{10})^{1/2}}\right)\frac{[\text{-CO-}]}{r^{1/2}} \qquad (17)$$

The lowering of the pH to 3 brings about the protonation of the ketomalonate dianion, i.e., a lower contribution of the substrate in its reactive form (reaction 11) as well as an increase in the rate of chain termination through protonation of the superoxide radical anion.[28] Accordingly at pH 3 (Figure 2) the chain reaction is very ineffective. The fact that it goes on at all is in line with the assumption that $HO_2^{\bullet-}$ which predominates at this pH exhibits some reactivity with respect to radical addition to the ketomalonic acid. At higher pH the intrinsic lifetime of $O_2^{\bullet-}$ is longer since it can only terminate according to reaction 10. Thus the chain reaction is more effective at higher pH.

The behavior of the chain reaction following a change in the temperature is noteworthy. Even though the equilibrium contribution of the carbonyl form increases from 10% at 20 °C to ≈60% at 70 °C according to our ^{13}C NMR data, the monoperoxyoxalic acid yield of a formate solution containing ketomalonic acid γ-irradiated at pH 10 remains practically unchanged when the temperature of the reaction system is raised from 20 to 70 °C. One reason might be that the increase in the proportion of the carbonyl form is offset mainly by the decrease in the ratio $k_{addition}/k_{reverse}$ which seems reasonable since the adducts **1a** and **1b** are in this sense analogous to the hydrate.

Final Remarks

Because of the intrinsically long lifetime of $O_2^{\bullet-}$ radicals, the interesting question arises as to whether such addition reactions occur with other systems as well and whether, on top of its well-documented transition-metal-ion-induced damaging properties to biological systems,[2] the type of reaction discovered here can contribute to the deleterious effects of $O_2^{\bullet-}$.

In fact, another chain reaction involving the $O_2^{\bullet-}$ radical has recently been discovered in our laboratory,[29] and work is in progress demonstrating the unexpected versatility of $O_2^{\bullet-}$-induced reactions in aqueous solutions. Again, radiation techniques are the methods of choice in their elucidation.

Registry No. $O_2^{\bullet}$, 11062-77-4; $^-$OCOCOCOO$^-$, 4004-36-8; $^-$OOCOCOO$^-$, 135189-92-3.

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Quantum Yields in the Photochemically Induced Radical Chemistry of Acyl Derivatives of Thiohydroxamic Acids

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Abstract: Acyl derivatives of *N*-hydroxyquinazoline-4-thiones are a novel source of disciplined carbon radicals. Quantum yield determination reveals that photolysis of these compounds initiates radical chains, resulting in quantum yields up to Φ = 60. Comparative studies with acyl derivatives of *N*-hydroxy-2-thiopyridone show that the quinazoline derivatives are more light-sensitive than the thiopyridone compounds. The carbon radicals thus formed from the former can be trapped selectively, without the formation of rearranged products (i.e. without the competition of the radicophilic thiocarbonyl group of the starting material with the radical trap).

Introduction

Radical chemistry has become an important tool in synthetic organic chemistry during the past 10–15 years.[1-10] This is related to the selectivity and mild reaction conditions associated with these reactions. The selectivity most often is a result of the disciplined

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nature[11] of these radicals. The latter, in turn, is a consequence of the effect of a suitable disciplinary group in the starting molecules.[12] The role of the thiocarbonyl group as such a moiety had been discovered in connection with the radical deoxygenation of secondary alcohols[13] in 1975 (Barton–McCombie reaction). Later this reaction was extended to primary[14,15] and tertiary alcohols[16] and diols.[17-23] With the introduction of some novel reagents,[24-29] many successful applications have been reported to date. The radical chemistry related to thiocarbonyl groups has recently been reviewed.[30]

Another important development was the conception of *O*-acyl thiohydroxamic acids as versatile sources of carbon radicals.[31] This group of compounds has become another valuable tool in synthetic radical chemistry, allowing the generation of carbon-centered,[32,33] as well as nitrogen-centered[34] and oxygen-centered, radicals.[35] Despite the plethora of successful applications, there has been little insight into the theoretical and quantitative background of the photochemistry of *O*-acyl-*N*-hydroxy-2-thiopyridone derivatives[36,37] and similar compounds.[38] We report here the results of our quantum yield studies related to the radical

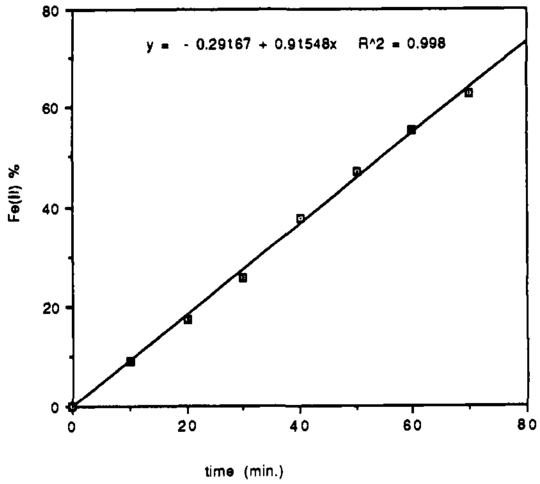

Figure 1. The photolytic conversion of Fe(III) oxalate to Fe(II) vs time. The light intensity was constant (1.35×10^{15} within $\pm 0.05 \times 10^{15}$ quanta/s).

Table I. Quantum Yields of Photolysis Products of Thiopyridone Derivatives **1b–d**

trap (5 equiv)	quantum yields[c,d] (Φ)		
	1b[a]	**1c**[a]	**1d**[b]
CCl_4	6[a,b] (24)[e]	23[b]	13
$CBrCl_3$	29 (24,[e] 55[e,f])	31	8
CBr_4	32	28	24
$(PhS)_2$	24 (8[g])	27	11
$(PhSe)_2$	14 (27[g])	19	10
$PhSO_2CH{=}CH_2$	35	34	22

[a] Solvent: CH_2Cl_2. [b] Solvent: $CDCl_3$. [c] Average of five experiments. [d] Unless otherwise stated, data obtained in 0.1 M solutions of the thiopyridone derivatives in the given solvents at 22 °C. [e] Trap as solvent. For CCl_4, this means 102.91 equiv of trap in the case of 0.1 M solution of **1b** in CCl_4. For $CBrCl_3$, this means 101.47 equiv of trap related to the 0.1 M of **1b** in $CBrCl_3$ solution. [f] Saturated solution of **1b** (0.771 M) in $CBrCl_3$ as solvent and trap. This means 13.16 equiv of the trap. [g] CH_2Cl_2 solution of **1b** (0.1 M) + 2 equiv (0.2 M) of trap. (The relative error of measurements is ±7%).

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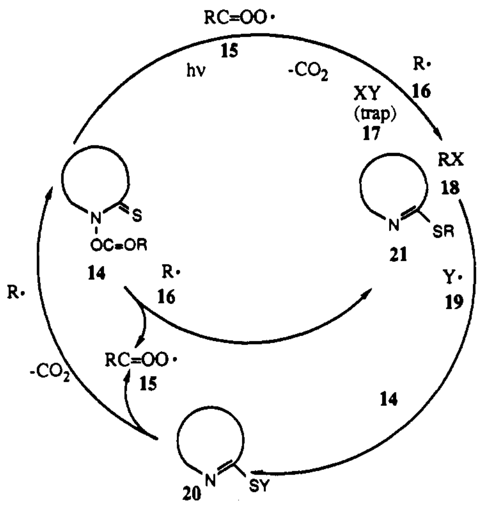
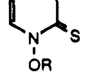
Scheme I



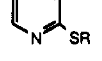
chemistry of *O*-acyl thiohydroxamic acid derivatives.

Results and Discussion

Synthesis of *O*-Acyl Thiohydroxamic Acids. *N*-Hydroxy-2-thiopyridone[39] (**1a**) was acylated either with the corresponding acid chloride or with *N,N'*-dicyclohexylcarbodiimide and the appropriate acid as described previously to give *O*-acyl derivatives **1b**,[40] **1c**,[40] **1d**,[40] and **1e**.[50c] The sulfides **2a**,[31b,h] **2b**,[41] **2c**,[42] **2d**,[42] **2f**,[40] **2g**,[40] and **2h** were prepared by the methods cited. The derivative **3b**[31e] of *N*-hydroxythiazoline-2-thione **3a**[31e] was prepared as before. The 2-substituted *N*-hydroxyquinazoline-4-thiones



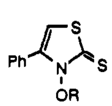
1a-e



2a-h

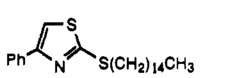
1a: R = H
1b: R = $CO(CH_2)_{14}CH_3$
1c: R = COC_6H_{11}
1d: R = $COC(CH_3)_3$
1e: R = COPh

2a: R = CCl_3
2b: R = CBr_3
2c: R = SPh
2d: R = SePh
2e: R = SPy (Py = 2-pyridyl-)
2f: R = $(CH_2)_{14}CH_3$
2g: R = C_6H_{11}
2h: R = $C(CH_3)_3$



3a, b

3a: R = H
3b: R = $CO(CH_2)_{14}CH_3$



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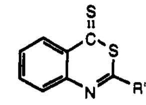
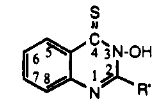
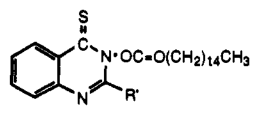
6a–c[44a–c] were synthesized from the benzothiazine derivatives **5a–c**.[43] The corresponding acyl derivatives **7a–c** are new compounds, synthesized by the acid chloride method from **6a–c** in high yields. These are highly light sensitive compounds and very easily rearrange into compounds of type **8**.[45a,b] Synthetic manipulations are best performed in a dark or semidark room. These compounds can be stored in a dark vial at −25 °C without decomposition. However, **7c** was too unstable even at this temperature in the dark. Within a few hours the rearranged product **9c** (R' = 4-methoxyphenyl) was observed in purified **7c**. Consequently this compound had to be studied as soon as it was prepared. For the same reasons **7c** was analyzed as **9c**.



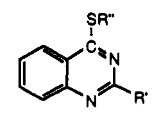
5a-c



6a-c



7a-c



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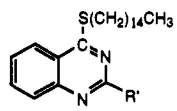
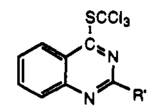


9a-c



10a-c

For **5, 6, 7, 9** and **10**: **a**: R' = Ph
b: R' = 1-naphthyl
c: R' = 4-OMePh

Photolysis Experiments. Quantum yields were determined with the use of an iron oxalate actinometer[46] with two types of filters.[47] Details are given in the Experimental Section. The light intensity, calculated in accordance with standard rules,[48] was $I = (1.35 \pm 0.05) \times 10^{15}$ quanta/s (Figure 1). As seen in Table I, acyl derivatives of **1a**, i.e. **1b–d**, were photolyzed in the presence of 5 equiv of a given radical trap in 0.1 M solutions at 22 °C. These data reveal that quantum yields for the *O*-acyl-*N*-hydroxy-2-thiopyridone derivatives studied varies between 6 and 35 (±7%), depending on the radical trap and the carbon radical involved. Since **1b** provides primary, **1c** secondary, and **1d** tertiary radicals, these figures indicate also the relative reactivity of these radicals toward the trap and the parent thiocarbonyl compound. An acyl thiohydroxamate (**14**, Scheme I), when photolysed, suffers homolytic cleavage between the N and O atoms, furnishing acyloxy radicals **15** and the thiyl radical observed earlier.[37] These acyloxy radicals decarboxylate when R is an aliphatic moiety but are more persistent in the case of aromatic and conjugated acids.[50] The radical chain thus initiated can continue, depending on the radical trap present. An excess of a good trap XY (**17**) can immediately react with the carbon radical **16**, resulting in the formation of the trapped product **18** and a chain-carrier radical **19**. The latter can react with another molecule of the starting **14**, giving **20** and the acyloxy radical **15**. This in turn can decarboxylate, furnishing the carbon radical **16**. The efficiency of a given trap, therefore,

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(52) (a) Sulfide, *tert*-butyl phenyl. (b) Selenide, *tert*-butyl phenyl. (c) Sulfide, cyclohexyl phenyl.

Table II. Quantum Yields of Photolysis Products of **1b** and **7a–c**

trap (5 equiv)[b]	quantum yields[a] (Φ) 1b	7a	7b	7c
$CBrCl_3$	27	60	34	54

[a] Average of five experiments (±7%). Data for 0.1 M $CDCl_3$ solutions at 22 °C. [b] Concentration of the trap in the reaction mixture before photolysis (0.5 M).

Table III. Half-Lives[a] of Acyl Derivatives **1b**, **7a–c**, and **3b**[b]

	1b	7a	7b	7c
$t_{1/2}$	200	19	23	21
	1b + 7a	**1b + 7b**	**1b + 7c**	**1b + 3b**
$t_{1/2}$ (of **1b**)	196	200	198	253
$t_{1/2}$ (of **7** or **3b**)	37	36	40	399

[a] Determined in 0.1 M $CDCl_3$ solutions. Photolysis: W light, 0 °C. $t_{1/2}$ in seconds. [b] For the mixed photolyses the $CDCl_3$ solutions were 0.1 M in both components.

depends on the concentration and reactivity ratios (of the thiocarbonyl group) of **14** and of trap XY, **17**. The radical chain is relatively long in the case of the known radical traps employed (up to 55 for **1b** and $CBrCl_3$). The relative reactivity of the thiocarbonyl group of **14** and the trap **17** is reflected by the ratio of the pyridine derivative **20**, formed from **14** and the radical Y• (**19**), and the rearranged product **21**. The disciplinary (thiocarbonyl) group is the best when the radical chain is selectively producing the trapped product **18** and the carbon radicals **16** are not consumed in unwanted side reactions with **14** or in any radical–radical process. Most of the quantum yields of acyl derivatives of the thiohydroxamic acid **1a** are in the range of 10–30 (Table I), indicating that the radical chain, once initiated, is effectively carried by the chain-carrying Y• radicals (**19**). These figures are indeed in accordance with the synthetic usefulness of these radical chain processes. Diphenyl diselenide absorbs light in the same region as the acyl derivatives; i.e. it acts as a filter in the solution. Thus, when 5 equiv is used, less light is available in the system than when 2 equiv of $(PhSe)_2$ is used (the light intensity being the same in both cases). This means in effect when 2 equiv of $(PhSe)_2$ is used, there is higher efficiency of N–O bond cleavage, and as our systems are only photolysed to 20% to keep concentration effects as constant as possible, we do not see the concentration effect of the trap going from 2 equiv to 5 equiv (Table I).

The reaction mixtures are easily analyzed by ^1H NMR, gas chromatography, and GC–MS methods with suitable internal references and authentic samples for identification. As shown in Table II, the novel *O*-acyl thiohydroxamic acid derivatives **7a–c** produce much higher quantum yields than the reference thiopyridone compound **1b**. With 5 equiv of $CBrCl_3$ as a trap, a quantum yield of Φ = 60 was achieved for the brominated product **11b**, indicating an efficient photoinitiated radical chain. The reactivity and light sensitivity of these novel thiohydroxamic acid derivatives **7a–c** are also reflected in their half-lives (Table III). There is 1 order of magnitude drop in their half-lives compared to that of the reference thiopyridone derivative **1b**. The half-life of this thiopyridone derivative **1b** (200 s) remains unchanged in the presence of **7a–c** and increases slightly (to 253) in the presence of the thiazoline derivative **3b**. The corresponding half-lives of the quinazolinethione derivatives **7a–c** were almost doubled in these competition experiments (determined by ^1H NMR in $CDCl_3$ solutions) but were still much lower than that of the corresponding reference compound **1b** (37–40 s). Despite their high reactivity as photoactive generators of carbon radicals, the thiocarbonyl groups of **7a–c** seem to be ideal disciplinary groups. This is indeed reflected in the fact that, in the presence of suitable traps, products of type **21** (Scheme I) cannot be detected, indicating that there is no competition between the trap and the starting **14** (here **7a–c**) for the carbon radical **16** (i.e. the latter behaves in a fully disciplined manner and the carbon radical R• is not consumed in unwanted side reactions). Thus, this selectivity allows the synthesis

Table IV. Photolysis Products of Acyl Derivatives **1b–d**, **3b**, and **7a–c**

product type[a]	substituent, R = $(CH_2)_{14}CH_3$	$C(CH_3)_3$	C_6H_{11}
RCl	**11a**[46]	**12a**[31h]	**13a**[46]
RBr	**11b**[46]	**12b**[46]	**13b**[46]
RSPh	**11c**[33]	**12c**[52a]	**13c**[52c]
RSePh	**11d**[33]	**12d**[52b]	**13d**[33]
$RCH_2(SPy)SO_2Ph$	**11e**[51]	**12e**[51]	**13e**[51]

[a] The products are all known compounds. GLC, ^1H NMR, and GC–MS has been used to identify these products. The corresponding data were compared with those of the authentic samples.

of the corresponding trapped products **11a–e**, **12a–e**, and **13a–e**, respectively, in high yields (>90%) in fast reactions (Table IV). It is also worth noting that the reaction conditions are extremely mild (0 °C or 22 °C, neutral solutions, short reaction times). This is compatible with (and tolerated by) a lot of sensitive functionalities found in natural products.

Products of the Radical Chain. Carriers, Chain Termination. Photolysis of *N*-hydroxy-2-thiopyridone palmitoate **1b** with visible light (tungsten light) in carbon tetrachloride solution gives (as expected) pentadecyl chloride (83%) (GLC, GC–MS).[31a,b] The corresponding chain-carrier radical (CCl_3•) reacts with the starting **14** (here **1b**) (Scheme I) giving a similar amount (82%) of 2-((trichloromethyl)thio)pyridine **2a**. The presence of dipyridyl disulfide (**2e**) indicates the role played by the photolytic initiation step. Its amount (0.7%), however, shows clearly that the radical chains, once initiated, are carried effectively by the chain-carrier trichloromethyl radical.[50] The presence of the expected rearrangement product, the thioether **2f** (9%), indicates that the trap is not good enough, i.e. the thiocarbonyl group of **1b** competes for the carbon radical **16** formed by the decarboxylation process from the acyloxy radical **15** (Scheme I). This thioether, in turn, can also act as a trap of carbon radicals, giving a ring-alkylated derivative of **2f** in 4%[53] yield. The rearranged compound **2f** is an unwanted, but chain-carrier, byproduct.

Photolysis of **1c** in $CDCl_3$ solution results in a more complicated picture. In the abscence of other effective chain carriers, the contribution of the photoproduct thiyl radical PyS• increases, indicating very short radical chains. Consequently, the yield of dipyridyl disulfide **2e** increases to 34% (almost 50-fold). The rearranged product thioether **2g** is present in 32% yield. The presence of ((trichloromethyl)thio)pyridine **2a** (3.6%),[50] cyclohexanol (3.7%), cyclohexanone (4.2%), cyclohexane, and cyclohexyl-2-(cyclohexylthio)pyridine (0.22%) indicate the termination steps. The oxygenated products are formed by the reaction of the carbon radical generated with the oxygen dissolved in $CDCl_3$ (the reaction itself was carried out under argon, but the solvent was not degassed).

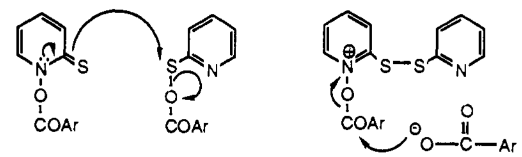
Low-Temperature Photolysis. Comparison of the photolysis of the thiohydroxamic acid acyl derivatives **1b** and **7b** at −60 °C with the trap bromotrichloromethane clearly demonstrated the superiority of this new group of compounds as a source of carbon radicals. Thus, photolysis of **1b** (0.1 M, $CDCl_3$, $CBrCl_3$ 5 equiv) at −60 °C for 20 min resulted in the formation of only 15% of the trapped product (bromopentadecane, **11b**) together with the rearranged product **2f** (8%); the remainder was the unreacted **1c** (77%). In contrast, when **7b** or **7c** (0.1 M, $CDCl_3$, $CBrCl_3$, 5 equiv) was photolyzed under the same conditions (−60 °C, 20 min), there was a quantitative conversion to the trapped product bromopentadecane **11b**, with no rearranged product **9b** or **9c**, respectively.

General Comment

In a recent article,[50c] Barton and Ramesh reported that photolysis of **1e** gave **22**. In contrast, an article by S. Z. Zard and his collaborators[35c] reported that **23** was first formed in a similar photolysis and that it disproportionated to give **24** and **25**. In

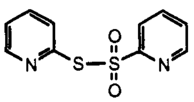
(53) Barton, D. H. R.; Zard, S. Z.; Castagnino, E.; Corsano, S. *Tetrahedron Lett.* **1986**, *27*, 6337–6338.

Scheme II

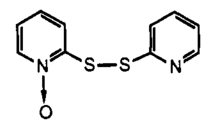


1e (Ar = Ph) 26 27

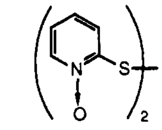
collaboration with Dr. A. I. Morrell, we repeated the photolysis of **1e** and confirmed the results reported by Zard et al. In addition, prompted by a helpful letter from Professor Fillmore Freeman (University of California, Irvine), we repeated our reported peracid oxidation of **25**, which was stated to give **22**. In fact, in spite of many efforts the disulfide **25** was resistant to peracid oxidation. The main features of the chemistry described[50c] are, however, correct. The formation of **23** and of acid anhydride (from nondecarboxylating aroyloxy radicals) can be explained by a nonradical mechanism (involving **26** and **27**) as indicated in Scheme II.



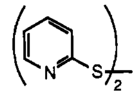
22



23



24



25

Conclusion

We can conclude that the quantum yields, determined for *O*-acyl-*N*-hydroxy-2-thiopyridone derivatives **1b–d**, are in accordance with their synthetic usefulness as a source of disciplined carbon radicals. These figures (Φ 10–30) indicate radical-chain lengths of synthetic value. We have demonstrated that the new acyl derivatives of the corresponding hydroxamic acids, on the basis of the *N*-hydroxyquinazolinethione structure, i.e. **7a–c**, are a more powerful source of disciplined carbon radicals. This is clearly indicated by quantum yields of up to $\Phi = 60$. Furthermore, the clean reaction mixtures indicate a delicately balanced reactivity of the disciplinary thiocarbonyl group of these new radical precursors. However, their photolytic half-lives (19–23 s) reflect both their great reactivity as well as their approach to the limit, where however, light sensitivity still allows (careful) synthetic manipulations.

The superiority of **7a–c** over **1b** as generators of radicals resides first in their 2-fold greater molar extinction coefficients, and second in the greater reactivity of the thiocarbonyl toward carrier radicals. This behavior is currently under investigation.

Experimental Section

General Procedures and Starting Materials. Melting points were determined with a Kofler hot-stage melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 881 spectrophotometer. ^{1}H and ^{13}C NMR spectra were determined for solutions in deuteriochloroform (unless specified otherwise) with a TMS internal reference on a Varian Gemini 200, Varian XL 200E, or Varian XL 400 instruments. Gas chromatography (glc) measurements were performed on a Chrompack Packard Model 439 gas chromatograph on 30-m capillary columns. GC–MS data were obtained on a Hewlett-Packard 5890 GC–MS system. Mass spectra were obtained on a VG Analytical 70S high-resolution double-focusing magnetic sector mass spectrometer with attached VG 11/250J data system in the EI or FAB mode. FAB spectra were obtained neat or in a glycerol matrix. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Solvents were used either as purchased or dried and purified by standard methodology. *N*-Hydroxy-2-thiopyridone was isolated from its sodium salt (Omadine). A 40% solution of the sodium salt of *N*-hydroxy-2-thiopyridone was a kind gift of the Olin Corp., Cheshire, CT. Other reference compounds and starting materials were purchased from Aldrich Chemical Co., Inc., Milwaukee, WI.

Photochemistry. Two types of filters were used for the photolysis experiments. The first filter was a chemical filter: a saturated aqueous solution of cobalt sulfate and an acetone (neat) filter,[48] both in 1-cm Pyrex glass photometer cuvettes. The other filter used was obtained from the Oriel Corp., Stratford, CT. This was a band-pass filter, 360 nm (Model 59810). The quantum yields were determined at 22 °C with a medium-pressure mercury lamp light source in a Rayonet apparatus (obtained from the Southern New England Ultraviolet Co.). The system used for quantum yield determination was checked by the use of an Optometrics Corp., Inc., Ayer, MA, 365 ± 5 nm interference filter (Catalog No. 02-3652, central wavelength 365 nm). The compound studied was 2,4,6-trimethyl-6-acetoxycyclohexa-2,4-dienone, prepared by a published procedure.[54a,b] This compound has a well-documented history of photochemistry[54c] and a known quantum yield ($\Phi = 0.53$ (365 nm, 20 °C))[55] at a specific concentration.[56] We observed only one isomer,[57] and we were able to reproduce this quantum yield (0.52).

General Procedure for Quantum Yield Determination. A standard solution of the acyl derivative was made in the particular solvent (0.1 M, usually 25 mL). Three-milliliter samples were removed by syringe and injected into five 1 cm × 1 cm photometer cells. These cells had already been flushed with argon (99.998% pure) (20 min) and were sealed with rubber septa and parafilm. A cell filled with a solution of iron(III) oxalate (0.006 M) was placed behind the sample cell. Before each set of measurements the light source was warmed up for 20 min so as to ensure a consistent light-intensity value. The light intensity was also measured before and during a given set of quantum yield measurements by using the iron oxalate actinometer. Five parallel samples were run and the yield of the trapped product (see Table I) determined by ^{1}H NMR with an appropriate internal standard. The conversion to the given trapped product was kept low (5–20%) so as to not upset the concentrations of the starting compounds.

Synthesis and Characterization of Starting Materials and Products. Compounds 1b–d. Acyl derivatives **1b–d** of *N*-hydroxy-2-thiopyridone (**1a**) were prepared as previously described.[40]

Compounds 2a–h. These compounds were identified by their ^{1}H NMR shifts and by GC–MS and compared with the data present in the literature.[31b,h,40,41,42]

Compounds 3a, 3b, 4. Known methods[31e] were used to prepare **3a** and **3b**. Compound **4** was identified by ^{1}H NMR and GC–MS. Its spectral data were compared with those given in the reference.[31e]

Compounds 5a–c and 6a–c. The method reported earlier[43,44a,b,c] was modified by avoiding the use of mercury salts. Instead, compounds of type **5** were recrystallized from methylene dichloride and ethanol. Thus, higher yields were obtained than reported.

Typical Procedures. The starting material for **5a**, (and thus **6a**), methyl *N*-benzoylanthranilate was prepared from methyl anthranilate (Aldrich) and benzoyl chloride and dried over P_2O_5 under vacuum (yield 95%, mp 99 °C, lit.[43] mp 100 °C).

2-Phenylbenzothiazine-4-thione (5a). Methyl *N*-benzoylanthranilate (10.3601 g, 40.5 mmol), phosphorus pentasulfide (18 g, 1 equiv), and freshly distilled dry pyridine (150 mL) were placed in a round-bottom flask equipped with a condenser and drying tube. The stirred solution was then immersed into an oil bath preheated to 140 °C and boiled for 18 h. Then the heating was stopped and the reaction mixture was poured on crushed ice. Once the ice melted, the precipitate was filtered, redissolved in methylene chloride, and dried with anhydrous magnesium sulfate. The solvent was then removed under vacuum and the resulting solid crystallized from methylene chloride/ethyl alcohol. The first two crops gave **5a** (9.0179 g, 73% (resulting in a 61% overall yield of **6a**), mp 122 °C, lit. mp 128 °C from benzene[43]).

2-Phenyl-3-hydroxy-3,4-dihydroquinazoline-4-thione (6a). Freshly distilled dry *p*-xylene (300 mL), methyl *N*-benzoylanthranilate (12.15 g, 47.6 mmol), and phosphorus pentasulfide (24.3 g, 54.7 mmol) were added to a two-neck round-bottom flask, previously flushed with dry argon and equipped with a reflux condenser connected to a calcium chloride drying tube. The solution was then brought to a boil and the reaction followed

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by TLC. After 10 h, the solution was allowed to cool to room temperature. The solution was filtered and the flask washed with benzene (300 mL) that was then also filtered. The organic solutions were combined and washed with sodium hydroxide solution (5%, 800 mL) two times and water (800 mL) also two times. The solvents were then evaporated, and the resulting solid was dried under vacuum over P_2O_5. The solid (**5a**) was then dissolved in a minimal amount of boiling ethanol and treated with hydroxylamine hydrochloride (3.5 g, 50 mmol) and sodium acetate (3.5 g, 25 mmol); both dissolved in the minimal amount of water. The red color of the solution changed to yellow in about 15 min and TLC indicated that there was no more **5a** present. Then the ethyl alcohol was evaporated under vacuum and **6a** was filtered and purified by repeated crystallization from ethyl alcohol. Overall yields: **6a** 33% (mp 143–144 °C, lit.[44a] mp 148 °C); **6b** 41% (181–182 °C, lit.[44a] mp 183 °C); **6c** 37% (mp 174 °C, lit.[44a] mp 173 °C). Pyridine can also be used as a solvent for the thionation step instead of *p*-xylene. When the solvent was pyridine, the workup was easier because benzene was not used to wash the solid that remained in the flask (see **5a** above).

Compounds 7a–c. Compounds of type **7** were prepared in the usual manner from palmitoyl chloride, **6**, and pyridine. The yields were almost quantitative. For quantum yield determinations the compounds were further purified by column chromatography. **7a**: mp 58 °C (CH_2Cl_2/hexanes); IR ($CHCl_3$, cm^{-1}) 2927, 1803, 1582, 1455, 1355, 1291, 1226, 1131, 863; UV-vis ($CHCl_3$) λ_{max1} = 356 nm, ϵ = 14290, λ_{max2} = 279 nm, ϵ = 15000; ^1H NMR ($CDCl_3$) δ 0.85 (m, 3 H), 1.2 (m, 24 H), 2.5 (m, 2 H), 2.2–2.6 (m, 2 H), 7.4–7.9 (m, 8 H), 8.75 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.02 (CH_3), 22.57, 23.97, 28.52, 28.90, 29.17, 29.24, 29.41 (CH_2 groups), 29.58 (5 × CH_2), 31.33 (CH_2), 31.80 (CH_2), 128.19 (2 × CH), 128.38 (CH), 128.44 (CH), 128.86 (2 CH), 129.97 (Cq), 130.64 (CH), 130.70 (CH), 131.81 (Cq), 134.71 (CH), 141.74 (Cq), 151.86 (Cq), 168.48 (C=O), 182.38 (C=S). Anal. Calcd for $C_{30}H_{40}N_2O_2S$: C, 73.13; H, 8.18; N, 5.69; S, 6.51. Found: C, 73.23; H, 8.20; N, 5.70; S, 6.48. **7b**: mp 65 °C (CH_2Cl_2/hexanes); IR ($CHCl_3$, cm^{-1}) 2928, 2855, 1805, 1589, 1463, 1346, 1319, 1296, 1262, 1049; UV-vis ($CHCl_3$) λ_{max1} = 355 nm, ϵ = 15000, λ_{max2} = 286 nm, ϵ = 15740; ^1H NMR ($CDCl_3$) δ 0.8–1.4 (m, 29 H), 1.9–2.3 (m, 2 H), 7.4–8.0 (m, 10 H), 8.79 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 23.7, 28.3 (br), 28.8, 29.0, 29.3, 29.4, 29.5, 29.6, 29.7, 31.1, 31.8, 124.7 (br), 126.5, 127.3, 127.4, 128.2, 128.6, 128.7, 130.2, 130.5, 130.7, 134.8, 141.7, 168.4, 182.3. Anal. Calcd for $C_{34}H_{42}N_2O_2S$: C, 75.24; H, 7.80; N, 5.16; S, 5.91. Found: C, 75.34; H, 7.86; N, 5.12; S, 6.02. **7c**: mp 61–62 °C (CH_2Cl_2/hexanes); IR ($CHCl_3$, cm^{-1}) 2928, 2854, 1805, 1587, 1463, 1253; UV-vis ($CHCl_3$) λ_{max1} = 358 nm, ϵ = 12540, λ_{max2} = 279 nm, ϵ = 19719; ^1H NMR ($CDCl_3$) δ 0.80–1.00 (m, 3 H), 1.10–1.65 (m, 26 H), 2.29–2.64 (m, 2 H), 3.87 (s, 3 H), 6.70–7.02 (m, 2 H), 7.49–7.59 (m, 1 H), 7.70–7.82 (m, 4 H), 8.68–8.76 (m, 1 H). Analyzed as **9c**.

Compounds 9a–c. **9a**: mp 53 °C; IR (CH_2Cl_2, cm^{-1}) 2927, 2854, 1611, 1532, 1480, 1339, 1305, 1125, 686; UV-vis (CH_2Cl_2) λ_{max} = 264 nm, ϵ = 34100; ^1H NMR ($CDCl_3$) δ 0.80–1.00 (m, 3 H), 1.20–1.70 (m, 24 H), 1.80–2.00 (m, 2 H), 3.45–3.52 (t, 2 H), 7.45–7.60 (m, 4 H), 7.76–7.86 (m, 1 H), 7.96–8.12 (m, 2 H), 8.59–8.68 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.10 (CH_3), 22.69, 29.17, 29.20, 29.29, 29.35, 29.60, 29.68, 31.91 (CH_2 groups) 122.66 (Cq), 123.82, 126.53, 128.43, 128.50, 129.03, 130.43, 133.44 (CH-s), 138.20 (Cq), 148.91 (Cq), 158.82 (Cq), 171.72 (Cq); MS (EI) 448 (M^+). Anal. Calcd for $C_{29}H_{40}N_2S$: C, 77.63; H, 8.99; N, 6.24; S, 7.15. Found: C, 77.64; H, 8.99; N, 6.19; S, 7.14. **9b**: mp 80 °C; IR ($CHCl_3$, cm^{-1}) 2927, 1524, 1471; UV-vis ($CHCl_3$) λ_{max} = 312 nm, ϵ = 19650; ^1H NMR ($CDCl_3$) δ 0.80–0.90 (m, 3 H), 1.0–1.5 (m, 24 H), 1.70–1.80 (m, 2 H), 3.35–3.45 (t, 2 H), 7.48–7.68 (m, 4 H), 7.80–8.20 (m, 6 H), 8.75–8.90 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.19 (CH_3), 22.76, 29.09, 29.27, 29.44, 29.47, 29.60, 29.65, 29.71, 29.75, 32.00 (CH_2 groups), 122.30 (Cq), 123.93, 125.26, 125.83, 126.44, 126.56, 127.04, 128.47, 129.14, 129.56, 130.31 (CH-s), 131.43 (Cq), 133.67 (CH), 134.25 (Cq), 136.56 (Cq), 148.76 (Cq), 161.55 (Cq), 171.37 (Cq). Anal. Calcd for $C_{33}H_{42}N_2S$: C, 79.48; H, 8.49; N, 5.62; S, 6.43. Found: C, 79.37; H, 8.50; N, 5.62; S, 6.42. **9c**: mp 79 °C; IR ($CHCl_3$, cm^{-1}) 2928, 2854, 1603, 1246; ^1H NMR ($CDCl_3$) δ 0.8–0.95 (m, 3 H), 1.2–1.6 (m, 24 H), 1.80–2.00 (m, 2 H), 3.46–3.53 (t, 2 H), 3.92 (s, 3 H), 7.02–7.10 (d, 2 H), 7.44–7.54 (m, 1 H), 7.74–7.86 (m, 1 H), 7.93–8.01 (m, 1 H), 8.04–8.12 (m, 1 H), 8.56–8.64 (d, 2 H). Anal. Calcd for $C_{30}H_{42}N_2OS$: C, 75.27; H, 8.84; N, 5.85; S, 6.70. Found: C, 75.41; H, 8.90; N, 5.90; S, 6.82.

Compounds 10a–c. A compound of type **7** was dissolved in methylene dichloride, and the flask was then sealed with a septum and flushed with argon (20 min). Five equivalents of bromotrichloromethane was added and the solution photolysed at room temperature until no **7** remained (5 min, TLC). Then the solvent was evaporated. The products crystallized upon addition of hexanes. **10a**: 85% yield; mp 107–108 °C; IR ($CHCl_3$, cm^{-1}) 3053, 1532, 1329, 980; UV-vis ($CHCl_3$) λ_{max1} = 331 nm, ϵ = 5350, λ_{max2} = 264 nm, ϵ = 33470; ^1H NMR ($CDCl_3$) δ 7.48–7.60 (m, 4 H), 7.80–7.90 (m, 2 H), 8.02–8.10 (m, 1 H), 8.72–8.80 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 93.5 (CCl_3), 121.3 (Cq), 122.2 (CH), 127.3 (CH), 128.6 (2 × CH), 128.9 (2 × CH), 129.5 (CH), 131.0 (CH), 134.3 (CH), 137.2 (Cq), 149.8 (Cq), 159.3 (Cq), 165.8 (CS). Anal. Calcd for $C_{15}H_9Cl_3N_2S$: C, 50.65; H, 2.55; N, 7.88; Cl, 29.90; S, 9.02. Found: C, 50.92; H, 2.61; N, 7.82; Cl, 29.75; S, 8.90. **10b**: 81% yield; mp 126 °C; IR ($CHCl_3$, cm^{-1}) 3009, 1609, 1541, 1479, 1316, 795; UV-vis ($CHCl_3$) λ_{max} = 317 nm, ϵ = 13720; ^1H NMR ($CDCl_3$) δ 7.5–7.70 (m, 4 H), 7.9–8.10 (m, 4 H), 8.14–8.22 (m, 1 H), 8.50–8.60 (m, 1 H), 9.14–9.24 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 93.64 (CCl_3), 121.12 (Cq), 122.52, 125.26, 125.90, 126.42, 126.90, 127.82, 128.48, 129.51, 130.91, 131.07 (CH-s), 131.24 (Cq), 134.21 (Cq), 134.46 (CH), 134.79 (Cq), 149.53 (Cq), 161.49 (Cq), 165.83 (Cq). Anal. Calcd for $C_{19}H_{11}N_2Cl_3S$: C, 56.25; H, 2.73; N, 6.91; Cl, 26.21; S, 7.90. Found: C, 56.33; H, 2.74; N, 6.92; Cl, 26.15; S, 7.81. **10c**: 97% yield; mp 152 °C; IR ($CHCl_3$, cm^{-1}) 3016, 1602, 1538, 1247, 1205, 719, 665; UV-vis ($CHCl_3$) λ_{max} = 300 nm, ϵ = 26090; ^1H NMR ($CDCl_3$) δ 3.91 (s, 3 H), 7.05–7.11 (d, 2 H), 7.50–7.60 (m, 1 H), 7.85–7.95 (m, 2 H), 8.05–8.13 (m, 1 H), 8.69–8.77 (d, 2 H). Anal. Calcd for $C_{16}H_{11}Cl_3N_2OS$: C, 49.83; H, 2.87; N, 7.26; Cl, 27.58; S, 8.31. Found: C, 49.77; H, 2.89; N, 7.20; Cl, 27.64; S, 8.25.

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