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Photochemical Synthesis. Conversion of *o*-Vinylthioanilides to Quinolines†

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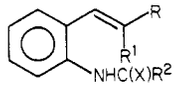
Quinoline derivatives are formed in fair to good yields when acetonitrile solutions of *o*-vinylthioanilides are irradiated with Pyrex-filtered light. The transformation is a singlet reaction and involves intramolecular cycloaddition of the thioamide, yielding unstable thietanes, as the initial step. In the case of *o*-(1-*trans*-propenyl)thioacetanilide (**2a**) the corresponding thietane has been detected by ^{1}H NMR spectroscopy by irradiating a toluene solution of the compound at −78 °C. The quantum yield of quinoline formation from **2a** appeared to be solvent dependent. Concomitant with quinoline formation, triplet cis–trans isomerization of the vinyl moiety takes place. In the case of **2a** the quantum yield for trans → cis isomerization is 0.506. A variable-temperature ^{1}H NMR study of 2,3-dimethylquinoline in toluene solution has also been performed. For the 2,3-dimethylquinoline–toluene complex the enthalpy and entropy of formation are −1.03 ± 0.10 kcal/mol and −3.7 ± 0.2 gibbs/mol, respectively.

Introduction

Whereas there has been a great deal of interest in the photochemistry of thiones over the past decade or so[1,2] few reports have dealt with the photochemical properties of thioamides. The first, published in 1967 by Grellmann and Tauer,[3] described the conversion of thiobenzanilide to 2-phenylbenzothiazole, a transformation involving an oxidative cyclization that has recently been utilized for the preparation of other benzothiazoles.[4] Later, Fourrey and others studied the photolysis of a variety of 4-thiouracil derivatives which were found to be reactive toward oxygen,[5] amines,[6] sodium borohydride,[7] alcohols,[8] and olefins.[9,10] Of these reactions, thioamide addition to carbon–carbon double bonds showed some generality.[11-14] It was, therefore, thought that it might be possible to induce an intramolecular cyclization reaction by excitation of styrene derivatives containing a thioamide moiety ortho to the olefinic substituent. This could ultimately lead to quinoline or indole derivatives (Scheme I). In fact, the former occurred, and the present paper describes our results.

Results

Preparation of Thioamides. The thioamides were synthesized from the corresponding amides (**1**), the preparations of which were variously carried out. Amides **1a** and **1b** were obtained in 17% total yield as a 6:1 mixture by a three-step synthesis from *o*-allylaniline. The compounds were separated by fractional crystallization. The stereochemistry of the isomers was assigned on the basis



1, X = O
2, X = S
a, R = R² = Me; R¹ = H
b, R = H; R¹ = R² = Me
c, R = Ph; R¹ = H; R² = Me
d, R = Me; R¹ = H; R² = Ph
e, R = CN; R¹ = H; R² = Me
f, R = CO_2Me; R¹ = H; R² = Me

† Contribution No. 199 from the Photochemistry Unit, London, Ontario, Canada.

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(6) (a) Fourrey, J.-L. *Tetrahedron Lett.* **1976**, 297. (b) Fourrey, J.-L.; Moron, J. *Ibid.* **1976**, 301.
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(10) (a) Fourrey, J.-L.; Jouin, P.; Moron, J. *Tetrahedron Lett.* **1973**, 3229. (b) Fourrey, J.-L.; Jouin, P.; Moron, J. *Ibid.* **1974**, 3005. (c) Fombert, C.; Fourrey, J.-L.; Jouin, P.; Moron, J. *Ibid.* **1974**, 3007. (d) Jouin, P.; Fourrey, J.-L. *Ibid.* **1975**, 1329.
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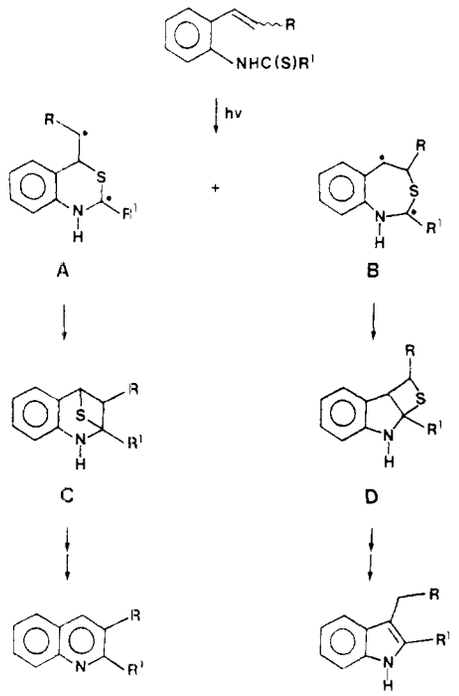
Scheme I



of their IR and NMR spectra; thus the major isomer gave rise to a strong absorption at 960 cm^{-1} in the infrared spectrum and a coupling constant of 16 Hz between the olefinic protons in the ^1H NMR spectrum, whereas the minor product exhibited a band at 760 cm^{-1} and a coupling constant of 10 Hz between the olefinic protons. The preparation of **1d** was performed in 54% yield by reduction of 1-nitro-2-(1-*trans*-propenyl)benzene with iron powder in glacial acetic acid and subsequent acylation of the resulting amine with benzoic anhydride. Finally, amides **1c** and **1e** were prepared by applying Heck's palladium-catalyzed olefin arylation[15] with *o*-bromoacetanilide. By this method arylation of styrene gave **1c** in 55% yield, whereas **1e** was obtained in 30% yield from acrylonitrile under the same conditions. The trans stereochemistry was assigned on the basis of a strong absorption near 960 cm^{-1} in the infrared spectra of both amides, and in the case of **1e** the assignment was further substantiated by a vicinal coupling constant of 16 Hz for the olefinic protons.

The synthesis of the thioamides was accomplished by treating the amides with equimolar amounts of phosphorus pentasulfide.[16] *o*-(1-*trans*-Propenyl)thioacetanilide (**2a**), *o*-(1-*cis*-propenyl)thioacetanilide (**2b**), and *trans*-*o*-styrylthioacetanilide (**2c**) were obtained in 44, 36, and 43% yield, respectively, from benzene solutions of the corresponding amides stirred at room temperature. In order to get a more satisfactory yield (38%) of *o*-(1-*trans*-propenyl)thiobenzanilide (**2d**), however, treatment of **1d** with P_2S_5 had to be performed in refluxing benzene. Owing to the low solubility of **1e** in benzene the preparation of *o*-(2-*trans*-cyanoethenyl)thioacetanilide (**2e**) was carried out in THF, but even then the yield was low (22%). In all cases the stereochemistry was proved by IR spectroscopy; all the trans isomers showed a strong absorption in the 950–975-cm^{-1} region, whereas **2b** gave rise to a band at 760 cm^{-1}.

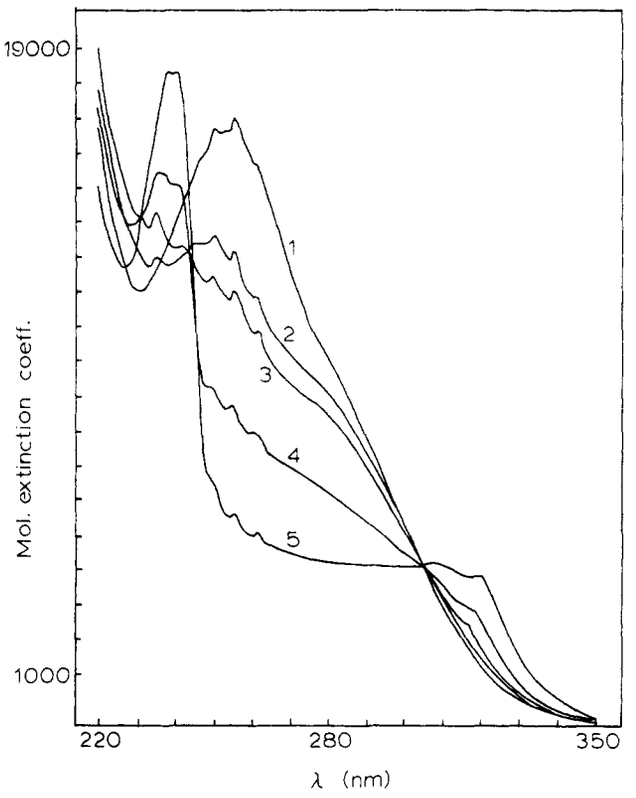
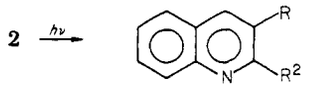


Figure 1. Sequential spectra from irradiation of a 4.5×10^{-5} M acetonitrile solution of **2a** at room temperature. Total irradiation times for scans 1–5 were 0, 8, 14, 33, and 93 min, respectively.

In the case of amide **1f**, on the other hand, treatment with P_2S_5 under a variety of conditions[16,17] failed to give any of the corresponding thioamide. Preparation of **2f** by palladium-catalyzed arylation[15] of methyl acrylate with *o*-bromothioacetanilide under a variety of conditions was also unsuccessful.

Irradiation of Thioamides at Room Temperature. Direct irradiation of acetonitrile solutions of thioamides **2a**, **2c**, **2d**, and **2e** through Pyrex at room temperature led to the formation of 2,3-dimethylquinoline (**3a**), 2-methyl-3-phenylquinoline (**3c**), 3-methyl-2-phenylquinoline (**3d**), and 3-cyano-2-methylquinoline (**3e**), respectively; the



3a, R = R^2 = Me
c, R = Ph; R^2 = Me
d, R = Me; R^2 = Ph
e, R = CN; R^2 = Me

compounds were isolated in fair to good yields by preparative TLC when the reactions were carried out on a preparative scale.[18] As indicated by the representative absorption spectrum which shows only one isosbestic point (Figure 1), the conversion from starting material to quinoline was not smooth and involved more than one absorbing substance. In two of the cases that unreacted starting material was isolated, spectroscopic analysis indicated that the recovered thioamide was contaminated with the corresponding cis isomer, the isolation of which in pure form, however, was successful only in a single case. Thus, *o*-(1-*cis*-propenyl)thioacetanilide was isolated by

(15) (a) Patel, A. B.; Ziegler, C. B.; Cortese, N. A.; Plevyak, J. E.; Zebovitz, T. C.; Terpko, M.; Heck, R. F. *J. Org. Chem.* **1977**, *42*, 3903. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

(16) Walter, W.; Bode, K. D. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 447.

(17) Scheeren, J. W.; Osmo, P. H. J.; Nivard, R. J. F. *Synthesis* **1973**, 149.

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preparative GLC after irradiation of **2a** to 50% conversion and was shown to be identical in all respects with an authentic sample.

Benzothiazole derivatives, which are potential products from photolysis of 2,[3,4] were not detected in any case.

Irradiation of 2a at Low Temperature. In order to gain more information about the course of quinoline formation, a dilute propionitrile solution of **2a**, kept at −78 °C in a spectrodewar, was irradiated, with a 450-W mercury arc, through a Pyrex filter permitting passage of light with $\lambda > 293$ nm. The reaction was monitored by UV spectroscopy which clearly showed that 2,3-dimethylquinoline, which gives rise to absorption maxima at 234, 303, and 315 nm (Figure 1), is not a primary photoproduct. On the other hand, when a solution of **2a** in propionitrile or acetonitrile was irradiated at −15 to −20 °C, under otherwise identical conditions, quinoline **3a** was formed during the course of irradiation. However, from the UV spectra the yield seemed in neither case to be comparable with that obtained at room temperature, and this suspicion was proved to be correct by a preparative experiment conducted at about −20 °C which yielded only 25% of **3a**; the main product was an intractable mixture of compounds with high molecular weights, the structures of which were not elucidated.

The involvement of at least one intermediate in the quinoline formation was indicated by an experiment monitored by NMR spectroscopy. A solution of thioamide **2a** in toluene-d_8, kept in a Pyrex NMR tube, was irradiated at −78 °C for 6 h and, after addition of cold chloroform-*d*, the ^{1}H NMR spectra of the reaction mixture were recorded at different temperatures between −70 and 40 °C. For comparison, NMR spectra of **2a** and **3a** in the same solvent mixture were run in the same temperature range. The high-field parts of the spectra contain the majority of the mechanistic information and are shown in Figure 2. From these spectra it appears that a thermally unstable compound, which gives rise inter alia to a singlet at 1.87 ppm and a doublet at 0.41 ppm, $J = 7.5$ Hz, in a ratio of 1:1, is formed during irradiation of **2a** at −78 °C. Since the disappearance of these signals parallels the appearance of the two singlets attributed to **3a**, we conclude that this compound is converted to 2,3-dimethylquinoline on warming. However, attempts to trap possible intermediates (vide infra) by addition of Raney nickel or sodium cyanoborohydride under appropriate conditions after irradiation were unsuccessful.

From the NMR spectra shown in Figure 2 it is uncertain whether or not 2,3-dimethylquinoline is formed to some extent during photolysis of **2a** even at −78 °C. The reason for this is that the chemical shifts of the singlets due to the two methyl groups of **3a** (denoted 2-Me and 3-Me) are so temperature dependent in the toluene-d_8–chloroform-*d* solvent mixture that the resonances are not distinguishable below −65 °C. These changes arise from formation of encountered complexes[19] between toluene-d_8 and **3a**, and we therefore undertook a variable-temperature NMR study of this quinoline. In order to enhance the solvent effect pure toluene-d_8 was used as solvent; tetramethylsilane was employed as internal standard. The results obtained are summarized in Table I. Furthermore, a plot of the solvent shift, $\Delta_{tol}^{CCl_4}$ ($\Delta_{tol}^{CCl_4} = \nu_{CCl_4} - \nu_{toluene\text{-}d_8}$ in hertz at 100 MHz), vs. temperature is shown in Figure 3; values for ν_{CCl_4}, which did not change significantly with temperature, were obtained from a solution of **3a** in carbon tetrachloride; this gave rise to singlets at 2.630 ppm (2-Me) and 2.431 ppm (3-Me) relative to internal Me_4Si.

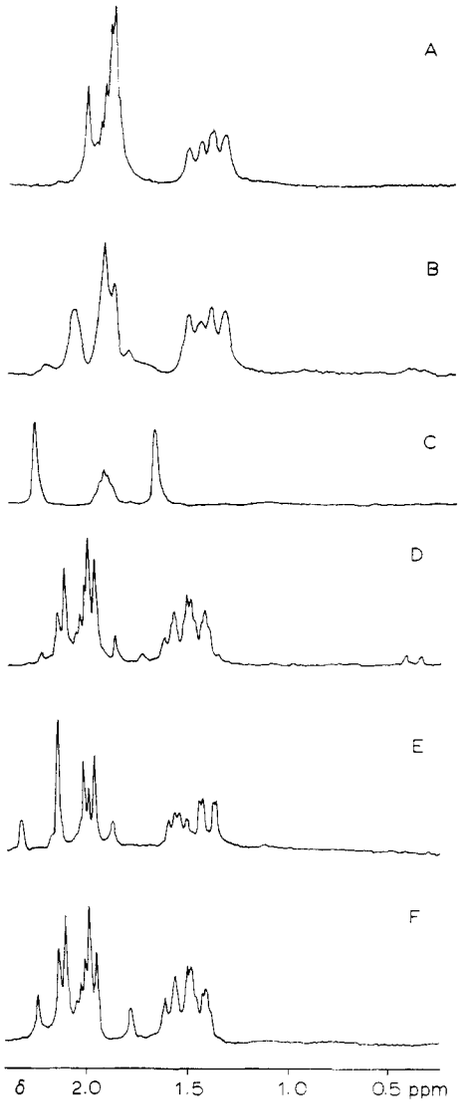


Figure 2. The high-field parts of ^{1}H NMR relevant to the irradiation of **2a** in toluene-d_8 at −78 °C. All spectra are run in a mixture of toluene-d_8 and chloroform-*d* (8:1). (A) **2a** at −50 °C; (B) reaction mixture at −50 °C; (C) **3a** at −50 °C; (D) reaction mixture at −40 °C; (E) reaction mixture at room temperature; (F) reaction mixture shown in spectrum E at −40 °C.

Table I. Variation of the Chemical Shifts of the Methyl Groups of 2,3-Dimethylquinoline with Temperature[a]

temp, °C	2-Me	3-Me
70	248.7	202.5
60	248.2	201.0
40	247.4	198.0
20	246.4	195.4
0	244.9	191.4
−20	243.7	187.5
−40	242.5	183.1
−50	242.0	181.0
−60	241.3	179.0

[a] Values refer to hertz at 100 MHz with tetramethylsilane as internal reference; determinations were carried out in a 3% w/v solution in toluene-d_8.

Quantum Yields. The photolysis of thioamide **2a** was studied in detail with respect to both 2,3-dimethylquinoline formation and trans → cis isomerization. The quantum yield of 2,3-dimethylquinoline formation in acetonitrile at room temperature was determined to be 0.0130 ± 0.0005 at 250, 278, and 306 ± 8 nm. Essentially the same values

(19) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: London, 1969; p 109, p 246.

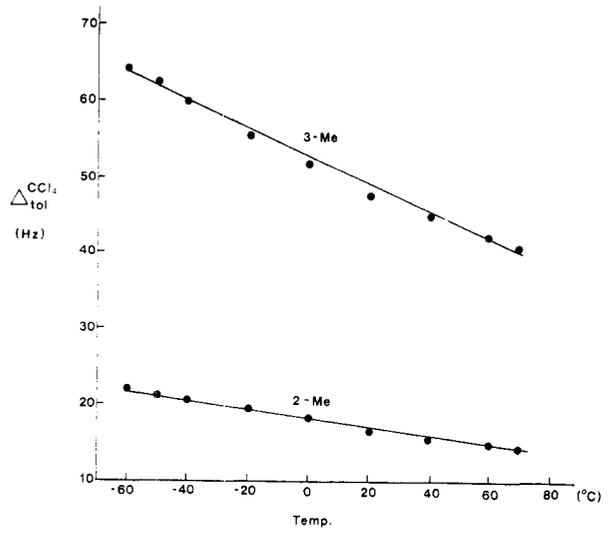


Figure 3. Temperature variation of the solvent shifts of the methyl groups (2-Me and 3-Me) of 2,3-dimethylquinoline.

Table II. Variation in Quantum Yield of 2,3-Dimethylquinoline Formation with Solvent at Room Temperature

solvent	ϵ^a	$\phi \times 10^2$
toluene	2.38	4.35
ether	4.34[b]	3.39
ethanol	24.58	2.75
methanol	32.70	1.85
acetonitrile	37.5[b]	1.30

[a] Dielectric constant at 25 °C unless otherwise stated. The values are taken from ref 22, pp 85-87. [b] Dielectric constant at 20 °C.

were obtained when the quantum yield was measured in the same solvent in the presence of varying amounts of the triplet quenchers ferrocene (E_T = 43 kcal/mol[20]) (0.0133 ± 0.0004) and 3,3,4,4-tetramethyldiazetine *N,N'*-dioxide (E_T < 42.4 kcal/mol[21]) (0.0135 ± 0.0004). On the other hand, addition of small amounts of acid or an increase in temperature resulted in a slight increase in the quantum yield; thus the quantum yield was 0.0161 ± 0.0004 in a 98:2 mixture of acetonitrile and glacial acetic acid at room temperature and 0.0261 ± 0.0005 in acetonitrile at 50 °C. The quantum yield of **3a** formation turned out to be solvent dependent, increasing from 0.0130 in acetonitrile to 0.0435 in toluene (Table II). Quinoline formation could not be induced by attempted sensitization with triphenylene (E_T = 66.5 kcal/mol[22]).

Quantitative measurements for the trans → cis isomerization were conducted in acetonitrile at room temperature by using 306 ± 8 nm irradiation, with the conversion of the starting material to the corresponding cis isomer kept at 2–3%. The quantum yield of *o*-(1-*cis*-propenyl)-thioacetanilide formation was determined to be 0.506 ± 0.008. The isomerization appeared to be quenched by ferrocene; the Stern–Volmer plot, shown in Figure 4 for quenching experiments conducted in acetonitrile, gives a line (r = 0.994) with slope $k_q\tau$ = 128 M^{-1}. Unfortunately accurate data for experiments resulting in more than 60% quenching could not be obtained owing to interference from ferrocene during the analysis.

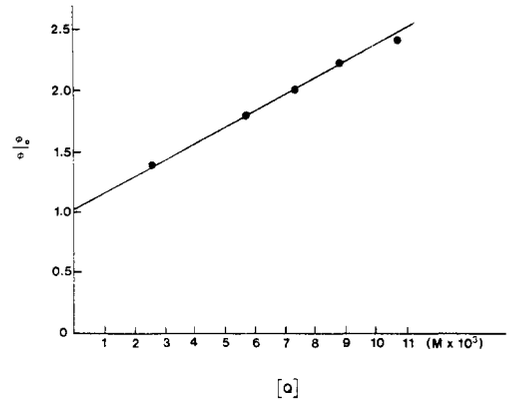


Figure 4. Stern–Volmer plot of ferrocene quenching of 2,3-dimethylquinoline formation in acetonitrile.

Discussion

From our results it is evident that the photochemistry of thioamides **2** is dominated by two processes: cis–trans isomerization and cyclization resulting, eventually, in formation of quinoline derivatives. Both processes take place whether the olefinic carbon–carbon double bond is electron deficient or electron rich, but the isomerization is the more efficient of the two processes as, in the case of **2a**, is reflected by a quantum yield of 0.506 for the trans → cis isomerization as compared with 0.013 for quinoline formation. However, the former does not consume thioamide and fair to good yields of quinolines are obtained. This photochemical transformation constitutes a new method for the preparation of quinoline derivatives. An interesting feature in the synthesis is that quinoline formation, in principle, takes place, by using, for instance, the Heck styrene route, by the combination of two moieties and an acylating agent, each of which may be substituted so as to introduce substituents specifically into the final ring system.

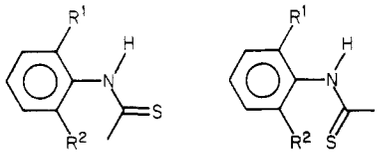
Quenching of the isomerization of **2a** by the triplet quencher ferrocene indicates that this reaction proceeds via a triplet intermediate, the lifetime of which is 1.6 × 10^{-8} s, on the assumption that the quenching rate constant in acetonitrile is 8 × 10^9 M^{-1} s^{-1}.[23] A linear Stern–Volmer plot for the isomerization quenching to ϕ_0/ϕ = 2.4 indicates that over 60% of the reaction pathway lies via triplet intermediates, but the restriction on increasing quencher concentration to increase this fraction means that we cannot exclude the possibility that some part of the isomerization may involve the singlet.

The isomerization could also be accounted for by a Schenck-like mechanism[24] involving, for instance, 1,4-biradical A (Scheme I), as such a species may be along the reaction pathway from starting material to a quinoline precursor. Such an intermediate could be capable of executing rotations about the carbon–carbon bond prior to C–S bond rupture, which would result in regeneration of the starting material and in the formation of the corresponding cis isomer.

Since the cyclization of **2**, which yielded quinolines, was unaffected by triplet quenchers and could not be sensitized by triphenylene, it seems likely that this transformation involves the singlet state. When the amide conformation

(20) Kikuchi, M.; Kikuchi, K.; Kokubun, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1331.
(21) Ullmann, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077.
(22) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 6.
(23) The value is calculated by dividing k_{diff} obtained from the Debye equation, 2.0 × 10^{10} M^{-1} s^{-1}, by 2.5, which is approximately the ratio between k_{diff} and k_q for solvents with a viscosity similar to that of acetonitrile. See: Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.
(24) Schenck, G. O.; Eggert, H.; Denk, W. *Justus Liebigs Ann. Chem.* **1953**, *584*, 176.

is as in 4, no reaction will occur and the excitation energy

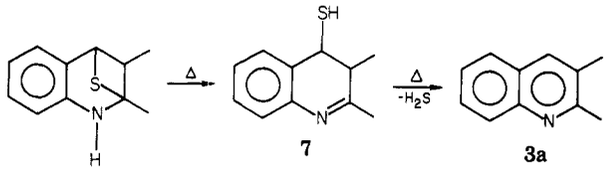


4 5

R^1, R^2 = H, CH=CHR
R = Me, Ph, CN

will be lost; if it is as in 5 (R^2 = CH=CHR, R^1 = H) intramolecular addition may take place, yielding, by analogy with thiones,[1] thioesters,[25] and thioamides,[11,12] a thietane (Scheme I). The required conformer has been shown to be present in solution (see below). Whether the addition is concerted (π,π^*) or proceeds (n,π^*) via biradical A (singlet, Scheme I; the alternative thiyl biradical is less likely) is unknown.

That the quinoline derivatives are formed via thietane intermediates is supported by the low-temperature irradiation of **2a** monitored by NMR spectroscopy. The clearly discernible singlet and doublet arising at 1.87 and 0.41 ppm, respectively, in the ^{1}H NMR spectrum of the solution during the photolysis are both compatible with the corresponding structure **6**. Further, **6** was converted



6 7 3a

to quinoline **3a** when the reaction mixture was allowed to attain room temperature; this was indicated by disappearance of the doublet at 0.41 ppm and the singlet at 1.87 ppm (Figure 2), by appearance of two singlets due to **3a**, and by concomitant loss of H_2S. Conceivably, **6** is converted to **3a** via thiol **7** which, however, is so easily aromatized by H_2S elimination that it cannot even be detected by NMR spectroscopy or trapped chemically by Raney nickel[13,26] or a slurry of sodium cyanoborohydride in acidic aqueous acetonitrile.[27]

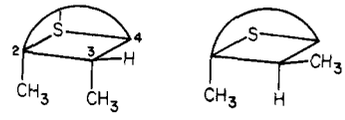
Another conclusion can be drawn from the NMR spectra in Figure 2: unless thietane **6** gives rise to a deceptively simple ^{1}H NMR spectrum, which is quite unlikely, the appearance of a single doublet in the 1.5–0.4-ppm region indicates that **6** is formed almost exclusively as a single isomer. The stereochemistry of the thietane can be assigned from the resonances that with certainty can be associated with this compound. The singlet at δ 1.87, due to the bridgehead methyl group, appears in a position which is as expected from NMR data for a variety of thietanes.[28] The methyl group in the 3-position, on the other hand, gives rise to a doublet at a substantially higher field than is usually the case for methyl groups attached to a thietane ring.[28] By analogy with benzopinane[29] and

Table III. Solvent and Temperature Effects on the Conformer Ratio of 2a[a]

	% s-cis isomer				
solvent	35 °C	10 °C	-30 °C	-40 °C	-50 °C
toluene-d_8	45.5				43.0
chloroform-d	39.6	39.5	40.3		40.5
acetonitrile-d_3	90.9	90.6	88.7	88.5	

[a] The assignments are based on the assumption that the singlets around 2.2 and 2.7 ppm are due to 4 and 5, respectively.[31]

1,4-methanonaphthalene derivatives,[30] which show significant shielding for groups syn to the benzene ring, the position of the doublet strongly indicates that the methyl group is situated syn to the benzene ring in **6**. Photolysis of **2a**, therefore, gives predominantly **6Z**, but the reason



6E 6Z

for the high degree of selectivity observed is not clear, particularly since the cycloaddition is believed to involve a biradical as a transient species.

Quinoline formation, at least in the case of **3a**, is temperature dependent. Although the quantum yield of 2,3-dimethylquinoline formation was measured only at 50 °C (ϕ = 0.026) and room temperature (ϕ = 0.013), it is evident from the chemical yields that the quantum yield continues to drop as the temperature is lowered below room temperature; thus the chemical yield of **3a** decreased from 69% at 25 °C to 25% at −20 °C when the reactions, except for the temperatures, were conducted to completion under otherwise comparable conditions.

One explanation of these observations could be that lowering the temperature results in accumulation of those thioamide conformers that are more prone to give products other than quinoline upon irradiation. However, this can be ruled out for two reasons. First, a study of the influence of temperature on solutions of **2a** with respect to the conformer composition, monitored by ^{1}H NMR spectroscopy, indicated that the temperature, in the temperature range of interest, had only a minor effect. This is substantiated by the fact that the NMR spectra appeared to change insignificantly between 35 and −50 °C in the solvents used and, furthermore, by the fact that the proportion of cis-thioamide **5** relative to the corresponding trans isomer **4**[31] in the same solvents hardly changed in the same temperature range (Table III). Secondly, it is reasonable to assume that if thioamide **2**, upon irradiation in acetonitrile, is consumed by reactions along pathways other than that leading to quinoline, e.g., by reaction with solvent,[32] similar thioamides like thioacetanilide (**8**) and thiocaproanilide (**9**) would be expected to be consumed when irradiated under identical conditions. However, experiments conducted with **8** and **9** under appropriate conditions showed that they were stable.

A third possibility is that thietane accumulates at low temperature and is destroyed photochemically because of the o-toluidine-type chromophore present.[33,34] Finally, the

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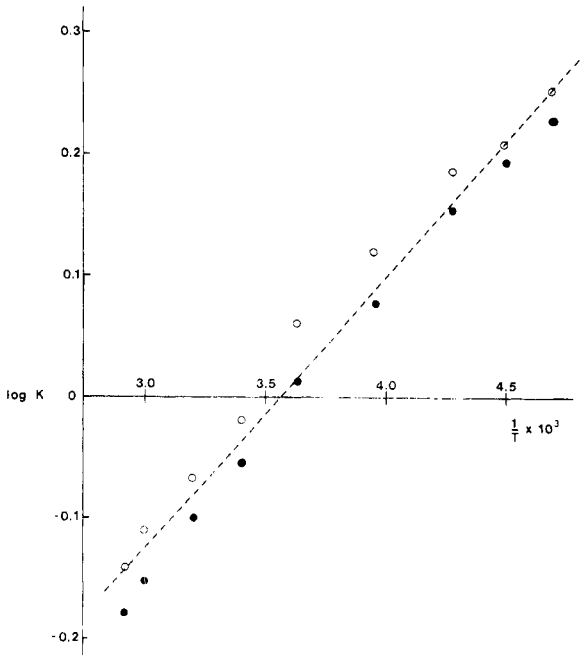

Figure 5. Plot of log K against $1/T$ based on data for the 2-Me (○) and 3-Me (●) resonances. The broken line results from a least-squares fit to all the points on the assumption of a linear fit.

interesting possibility remains that the photochemical step requires thermal activation.

A variable-temperature NMR study of **3a** requires some comment. From the results presented in Table I and Figure 3 it is clear that collision complex formation takes place when **3a** is dissolved in toluene and this association, described by eq 1, is favored as the temperature is lowered.

$$\text{quinoline} + \text{toluene} \rightleftarrows [\text{quinoline–toluene}] \quad (1)$$

The temperature variation of the equilibrium constant, K, for eq 1 provides a means of evaluating the enthalpy and entropy of formation, ΔH and ΔS, respectively, for the complex on the basis of an assumed 1:1 association. Thus, Abraham[35] has shown that if a fraction, p, of the solute molecules is complexed, eq 2 relates K to ΔH and ΔS. The value of p at any temperature, t, can be calculated from eq 3[36] where, for the resonance due to a particular proton,

$$K = p/(1 - p) = e^{\Delta S/R - \Delta H/RT} \quad (2)$$

$$p = \nu_t/\nu_c \quad (3)$$

ν_c is the chemical shift in the pure complex and ν_t is the chemical shift observed at a temperature, t. Both ν_c and ν_t are measured relative to the chemical shift of the resonance under consideration in the absence of complexation, in this case the chemical shift in carbon tetrachloride. By extrapolation of the lines shown in Figure 3 to 0 K, ν_c is estimated to be 102 ± 5 Hz for 3-Me and 34 ± 2 Hz for 2-Me. By use of eq 2 and eq 3, plots of log K against $1/T$ were then obtained for the 2-Me and 3-Me singlets (Figure 5). Within experimental error, the points can be represented by a common line which gave $\Delta H = -1.03 \pm 0.10$ kcal/mol and $\Delta S = -3.7 \pm 0.2$ gibbs/mol for the complex formation. These values are of the same order of magnitude as those found for complexes between toluene and other solutes, e.g., methyl iodide,[35] iodoform,[35] and 5α-androstan-11-one.[36]

Experimental Section

General Techniques. ^{1}H NMR spectra were run in $CDCl_3$ (unless otherwise noted) on either a Varian T-60 instrument or a Varian XL-100 spectrometer. The chemical shifts are reported in δ values relative to tetramethylsilane which was used as internal standard. Mass spectra were obtained on a Varian MAT 311A mass spectrometer at an ionization potential of 70 eV. A column of 5% FFAP on Chromosorb W 80/100 (5 ft × $^1/_8$ in.) was used for GLC. Benzophenone was used as internal standard for quantitative measurements. Preparative GLC was carried out by using a column of 15% FFAP on Chromosorb W 80/100 (6 ft × $^1/_4$ in.). Merck silica gel 60 GF_{254} was used for TLC analyses. Melting points and boiling points are uncorrected.

Solvents. Propionitrile (Aldrich) was distilled twice from calcium hydride. Tetrahydrofuran (THF) (Spectro, Caledon Lab) was distilled under N_2 from sodium wire in the presence of benzophenone. Acetonitrile (Aldrich Gold Label) was used without further purification, as were tetrachloromethane, methanol, cyclohexane Fisher Spectranalyzed Grade), and ethanol (absolute). Acetonitrile-d_3, chloroform-d, and toluene-d_8 from Merck, Sharp, and Dohme were used as solvents for NMR samples.

Irradiations. Preparative irradiations were performed with a Hanovia 450-W medium-pressure mercury arc. Quantum yield measurements, sensitized reactions, and quenching experiments were carried out on a JASCO CRM-FA spectroirradiator; ferrioxalate actinometry was used.[37] Unless otherwise stated all samples were degassed to a residual pressure of 2–3 × 10^{-5} mmHg by the freeze–pump–thaw method prior to irradiation.

Sensitizer and Quenchers. Triphenylene (Aldrich) was used without further purification. 3,3,4,4-Tetramethyldiazetine N,N'-dioxide was prepared as described by Greene and Gilbert[38] and recrystallized from methanol, mp 186–188 °C dec (lit.[38] mp 190–192 °C dec). Ferrocene, synthesized according to Wilkinson,[39] was purified by sublimation to give orange needles, mp 171–173 °C (lit.[39] mp 173–174 °C).

Preparation of Amides. *o*-(1-Propenyl)acetanilide (1a and 1b). A solution of 2.40 g (18 mmol) of *o*-allylaniline[40] in 10 mL of a 0.50 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol was stirred under nitrogen at 50 °C for 16 h. After the solution was cooled, brine (25 mL) was added and the resulting solution was extracted with ether; the ether extracts were combined, washed with brine, and dried (Na_2SO_4). Evaporation of the ether left 2.35 g of a yellow liquid which was immediately treated with 1.4 mL of acetic anhydride. After a while a solid formed. NaOH (1.0 M, 10 mL) was added and the solid was filtered and washed with water. Recrystallization from petroleum ether/chloroform (4:1) gave 1.92 g (61%) of pure *o*-(1-*trans*-propenyl)acetanilide (**1a**) as white needles: mp 124–125 °C; UV (CH_3OH) λ_{max} 219 nm (ε 18 000), 251 (16 000); IR (Nujol) 3200, 1650, 1570, 1540, 1300, 1110, 1040, 1010, 960 cm^{-1}; ^{1}H NMR δ 1.86 (d, 3 H, J = 5 Hz), 2.10 (s, 3 H), 5.70–6.63 (m, 2 H), 6.86–7.46 (m, 4 H), 7.55 (br s, 1 H, NH); mass spectrum, m/e (relative intensity) 175 (11), 133 (23), 132 (100), 118 (38), 117 (29); exact mass, calcd for $C_{11}H_{13}NO$ 175.09970, found 175.09995.

The filtrate after recrystallization of **1a** was concentrated and 33 mg (10%) of *o*-(1-*cis*-propenyl)acetanilide (**1b**) was isolated by preparative TLC by using ether as eluant: mp 98 °C; UV (CH_3OH) λ_{max} 250 nm (ε 10 700), 320 (900); IR (Nujol) 3300, 1655, 1580, 1540, 1290, 760 cm^{-1}; ^{1}H NMR δ 1.73 (m, 3 H), 1.85 (s, 3 H), 5.66–6.65 (m, 2 H), 6.83–7.56 (m, 4 H), 8.13 (br s, 1 H, NH); mass spectrum, m/e (relative intensity) 175 (14), 133 (22), 132 (100), 118 (38), 117 (28); exact mass, calcd for $C_{11}H_{13}NO$ 175.09970, found 175.09995.

***o*-*trans*-Styrylacetanilide (1c).** A mixture of 1.464 g (6.84 mmol) of *o*-bromoacetanilide, 0.801 g (7.71 mmol) of styrene, 0.780

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g (7.71 mmol) of triethylamine, 0.164 g (0.54 mmol) of tri-o-tolylphosphine, and 0.013 g (0.06 mmol) of palladium acetate in 3 mL of dry xylene was heated at 100 °C under nitrogen. After 6.5 h additional portions of palladium acetate (0.065 g, 0.29 mmol) and tri-o-tolylphosphine (0.318 g, 1.05 mmol) were added and the mixture was heated for another 2.5 h. The brown reaction mixture was then poured into water and extracted with ether. Evaporation of the ether left a residue from which 0.900 g (55%) of pure **1c** was isolated by preparative TLC (silica gel, ether), mp 140 °C (lit.[41] mp 140 °C).

***o*-(1-*trans*-Propenyl)benzanilide (1d).** To a refluxing solution of 3.15 g (20 mmol) of *trans*-1-(*o*-nitrophenyl)prop-1-ene[42] in a mixture of 115 mL of glacial acetic acid and 115 mL of absolute ethanol was added 4.70 g (85 mmol) of iron powder. The resulting mixture was refluxed for 4 h after which it was made basic by addition of sodium carbonate and filtered. The filtrate was extracted with hexane; the hexane fractions were combined, washed with water, and dried over $MgSO_4$. The solvent was evaporated to leave 2.0 g of a yellow oil which was mixed with 12.5 mL of 10% aqueous NaOH and 2.1 mL of benzoyl chloride. The mixture was shaken and after 10 min the liquid solidified. The solid was filtered and recrystallized from methanol to give 2.57 g (54%) of pure **1d**: mp 165–166 °C; UV (CH_3OH) λ_{max} 235 nm (ϵ 22600); IR (Nujol) 3260, 1650, 1600, 1580, 1525, 1300, 1075, 1025, 965 cm^{-1}; ^1H NMR δ 1.83 (m, 3 H), 5.66–6.66 (m, 2 H), 6.93–8.10 (m, 10 H); mass spectrum, *m/e* (relative intensity) 237 (6), 132 (89), 117 (15), 106 (84), 78 (100); exact mass, calcd for $C_{16}H_{15}NO$ 237.115355, found 237.115080.

***o*-(2-*trans*-Cyanoethenyl)acetanilide (1e).** A mixture of 1.962 g (9.17 mmol) of o-bromoacetanilide, 0.534 g (10.4 mmol) of acrylonitrile, 1.017 g (10.0 mmol) of triethylamine, 0.445 g (1.50 mmol) of tri-o-tolylphosphine, and 0.112 g (0.50 mmol) of palladium acetate in 2 mL of dry xylene was kept under nitrogen at 100 °C for 4 h. Volatile components were then distilled off and the residue was mixed with water and extracted with ether. Evaporation of the ether left a yellow solid which was recrystallized from benzene to give 0.511 g (30%) of **1e**, mp 175 °C (lit.[43] mp 172–174 °C).

Preparation of Thioamides 2a, 2b, 2c, and 2d. General Procedure. To a solution of amide in dry benzene (about 30 mL/mmol of amide) was added 1 molar equiv of P_2S_5. The resulting mixture was stirred at room temperature (in the cases of **1a**, **1b**, and **1c**) or refluxed (in the case of **1d**) until the reaction was complete (~4 h) as indicated by TLC (silica gel, pentane/ether (1:1)). The reaction mixture was filtered, leaving a solid material which was washed with benzene and filtered before being discarded. The combined filtrate was concentrated to give an oily residue from which the corresponding thioamide was separated by preparative TLC.

***o*-(1-*trans*-Propenyl)thioacetanilide (2a)** was obtained as white needles in 44% yield after chromatography (silica gel, pentane/ether (1:1)): mp 91 °C; UV (CH_3OH) λ_{max} 256 nm (ϵ 16900), 280 (10200) (shoulder); IR (Nujol) 3160, 1530, 1245, 1170, 970 cm^{-1}; ^1H NMR δ 1.90 (m, 3 H), 2.33 and 2.74 (2 s, total 3 H, $CSCH_3$), 6.00–6.60 (m, 2 H), 7.00–7.70 (m, 4 H), 8.70 and 9.44 (2 br s, total 1 H, NH); mass spectrum, *m/e* (relative intensity) 191 (8), 176 (22), 158 (100), 150 (21), 143 (24), 130 (19), 115 (42); exact mass, calcd for $C_{11}H_{13}NS$ 191.07686, found 191.07663.

***o*-(1-*cis*-Propenyl)thioacetanilide (2b)** was isolated as a pale yellow oil in 36% yield by preparative TLC (silica gel, pentane/ether (1:1)): UV (CH_3OH) λ_{max} 236 nm (ϵ 10300), 276 (8900); IR (film) 3200, 3020, 1530, 1450, 1380, 1160, 900, 760 cm^{-1}; ^1H NMR δ 1.76 (2 sets of dd, total 3 H), 2.41 and 2.72 (2 s, total 3 H, $CSCH_3$), 5.80–6.20 (m, 1 H), 6.30–6.50 (m, 1 H), 7.10–7.50 (m, 4 H), 8.62 and 9.37 (2 br s, total 1 H, NH); mass spectrum, *m/e* (relative intensity) 191 (9), 176 (25), 158 (100), 150 (21), 143 (18), 132 (16), 115 (23); exact mass, calcd for $C_{11}H_{13}NS$ 191.07686, found 191.07681.

***o*-*trans*-Styrylthioacetanilide (2c)** was obtained as a white powder in 43% yield by preparative TLC (silica gel, pentane/ether (1:1)): mp 119 °C; UV (CH_3CN) λ_{max} 225 nm (ϵ 25800), 286 (36700), 310 (33000) (shoulder); IR (Nujol) 3200, 1520, 1260, 1230, 1160, 950 cm^{-1}; ^1H NMR δ 2.30 and 2.70 (2 s, total 3 H, $CSCH_3$), 6.83–7.83 (m, 11 H), 9.01 and 9.83 (2 br s, total 1 H, NH); mass spectrum, *m/e* (relative intensity) 253 (10), 221 (19), 220 (100), 188 (23), 186 (32), 152 (18), 114 (56), 118 (20); exact mass, calcd for $C_{16}H_{15}NS$ 253.092515, found 253.092256.

***o*-(1-*trans*-Propenyl)thiobenzanilide (2d)** was isolated as crystals in 38% yield by preparative TLC (silica gel, pentane/ether (5:1)): mp 127 °C; UV (CH_3OH) λ_{max} 245 nm (ϵ 25300), 300 (6800) (shoulder); IR (Nujol) 3200, 1510, 1242, 1220, 1002, 975 cm^{-1}; ^1H NMR δ 1.86 (dd, 3 H), 6.00–6.64 (m, 2 H), 6.80–8.20 (m, 9 H), 8.90 (br s, 1 H, NH); mass spectrum, *m/e* (relative intensity) 253 (8), 238 (21), 220 (81), 212 (20), 121 (100), 115 (39); exact mass, calcd for $C_{16}H_{15}NS$ 253.092515, found 253.092870.

Preparation of *o*-(2-*trans*-Cyanoethenyl)thioacetanilide (2e). A mixture of 0.56 g (3.0 mmol) of **1e** and 0.67 g (3.0 mmol) of P_2S_5 in 20 mL of dry THF was stirred at room temperature for 2.5 h and then filtered. The filtrate was diluted with 80 mL of ether, shaken with 5% aqueous $NaHCO_3$ (2 × 30 mL) and water (30 mL), and dried (Na_2SO_4). The solvent was then evaporated and the residue separated by preparative TLC (silica gel, pentane/ether (1:1)) to give, after recrystallization from benzene/pentane (1:1), 0.136 g (22%) of **2e** as pale yellow crystals: mp 121–122 °C; UV (CH_3OH) λ_{max} 224 nm (ϵ 12300) (shoulder), 232 (10100) (shoulder), 270 (14000); IR (Nujol) 3250, 2210, 1580, 1500, 1212, 1119, 960 cm^{-1}; ^1H NMR δ 2.30 and 2.73 (2 s, 3 H, $CSCH_3$), 5.80 (d, 1 H, J = 16 Hz), 7.06–7.66 (m, 5 H), 8.80 and 9.46 (2 br s, 1 H, NH); mass spectrum, *m/e* (relative intensity) 202 (21), 169 (90), 162 (100), 150 (31), 144 (80), 141 (26), 134 (31), 118 (48), 117 (57); exact mass, calcd $C_{11}H_{10}N_2S$ 202.05646, found 202.05648.

Preparative Irradiation. 2a. A solution of 107 mg of **2a** in 60 mL of acetonitrile in a sealed Pyrex tube was irradiated at room temperature for 3.5 h. Removal of the solvent left a yellow oil which consisted of at least five products and some polymeric material according to GLC (column temperature 120–170 °C) and TLC (silica gel, ether/pentane (1:3)) analyses. The compounds were separated by preparative TLC (same conditions), but only one of the products was identified, 2,3-dimethylquinoline (**3a**): yield 61 mg (69%) of pale yellow crystals; mp 63–65 °C (lit.[44] mp 65 °C). The quinoline was precipitated as a picrate and recrystallized from ethanol; mp 228 °C (lit.[45] mp 229 °C).

When a solution of **2a** (155 mg) in acetonitrile (330 mL), deoxygenated by bubbling N_2 through for 2 h, was kept under nitrogen in a Pyrex vessel at −19 to −28 °C and irradiated until the thioamide had been consumed (5 h) as indicated by TLC (silica gel, ether), 32.4 mg (25%) of **3a** was isolated by preparative TLC (same conditions).

In another experiment, conducted to approximately 50% conversion, unreacted thioamide was isolated in addition to **3a**. The NMR and IR spectra of the thioamide showed peaks due to both **2a** and **2b** which were separated by preparative GLC (column temperature 170–175 °C) and proved to be identical with authentic samples of **2a** and **2b**, respectively.

2c. A solution of **2c** (41 mg) in acetonitrile (20 mL) was kept in a sealed Pyrex tube and irradiated at room temperature for 8 h. The solvent was evaporated to give a yellow oil which was a mixture of at least seven compounds and some polymeric material according to TLC analysis (silica gel, ether/pentane (1:3)). The compounds were separated by preparative TLC (same conditions), but only two of them were identified, starting material, yield 15 mg (37%), and 2-methyl-3-phenylquinoline (**3c**), yield 10 mg (44% based on consumed **2c**) as an oil. The quinoline was precipitated as a picrate and recrystallized from ethanol/acetonitrile (1:1); mp 166–168 °C (lit.[44] mp 164 °C).

2d. A solution of **2d** (143 mg) in acetonitrile (65 mL) was kept in a sealed tube and irradiated at room temperature for 27 h. Evaporation of the solvent left a yellow residue which consisted of at least five compounds and some polymeric material according to TLC analysis (silica gel, benzene). Isolation by preparative TLC (same conditions) afforded 63 mg (44%) of starting material and 40 mg (58% based on consumed **2d**) of 3-methyl-2-phenylquinoline (**3d**), mp 48–49 °C (lit.[46] mp 52–53 °C). The quinoline was precipitated as a picrate and recrystallized from methanol;

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mp 208–209 °C (lit.[44] mp 208 °C).

2e. A sample of **2e** (115 mg) in acetonitrile (65 mL) was kept in a sealed Pyrex tube and irradiated at room temperature for 25 h. The solvent was evaporated to give an oil which was a mixture of at least four compounds and some polymeric material as evidenced by GLC (160 °C) and TLC (silica gel, ether/pentane (1:1)) analyses. Isolation by preparative TLC (same conditions) gave 59 mg (51%) of starting material and 22 mg (46% based on consumed **2e**) of 2-methyl-3-cyanoquinoline (**3e**), mp 121–128 °C (lit.[47] mp 131 °C). The quinoline was converted to the corresponding picrate, mp 204–205 °C dec (lit.[48] mp 208 °C). The NMR and IR spectra of the recovered thioamide showed bands, in addition to those due to **2e**, which can be ascribed to *o*-(2-*cis*-cyanoethenyl)thioacetanilide; however, the latter isomer could not be isolated by TLC or GLC.

Irradiation of 2a Followed by Spectroscopy. The reactions were performed on the optical bench system described previously,[49] by using a Pyrex filter permitting the passage of light $\lambda > 293$ nm.

UV. When the reaction was followed by UV spectroscopy the sample was irradiated in a quartz spectrodewar which allowed cooling to appropriate temperature. The sample cell was situated in an envelope equipped with two windows parallel to those of the cell and the envelope was evacuated to prevent condensation on the surface of the cell. The sample was cooled by adding appropriate coolant to the Dewar, i.e., ice/sodium chloride (3.3:1) (−15 to −20 °C) and carbon dioxide/ethanol (−78 °C). Before the irradiation started the sample was kept at bath temperature for 1 h. Irradiations at room temperature and −15 to −20 °C were performed in propionitrile and acetonitrile whereas photolysis at −78 °C was carried out in propionitrile. UV spectra were recorded at intervals during the irradiations (Figure 1).

NMR. A solution of **2a** (11.1 mg) in toluene-d_8 (0.40 mL), kept in a Pyrex NMR tube, was immersed near the wall of a Pyrex beaker containing ethanol–carbon dioxide. The probe tube was kept at −78 °C in the dark for 20 min and was then photolyzed for 6 h at the same temperature. Condensation on the outer wall of the beaker was prevented by blowing air along the wall. During the photolysis some of the thioamide crystallized but most of the crystals dissolved when approximately 0.05 mL of chloroform-*d*, precooled to −60 °C, was added after the irradiation. The resulting mixture, still kept at −78 °C, was then examined by NMR spectroscopy at variable temperatures, starting at −70 °C, going stepwise up to 40 °C, and then down to −70 °C again. For comparison the NMR spectra of **2a** and **3a** in the same solvent mixture were recorded at different temperatures. Parts of some of the NMR spectra are shown in Figure 2.

A variable-temperature NMR study of **3a** in pure toluene-d_8 with tetramethylsilane as internal standard was also carried out; the most significant results are presented in Table I and Figure 3.

Quantum Yields. Direct photolysis quantum yields were determined for 2,3-dimethylquinoline (**3a**) and *o*-(1-*cis*-propenyl)thioacetanilide (**2b**) formation. Analysis was carried out by GLC; the column temperature was 120 °C in the case of **3a** analysis and 165 °C in the case of **2b** analysis. Irradiations were conducted to about 1% conversion for the analysis of **3a** and 2–3% conversion for the analysis of **2b**. Values quoted are averages of 2–4 determinations. The quantum yield of **3a** formation was determined in toluene, ether, ethanol, methanol, acetonitrile, and acetonitrile/acetic acid (98:2). When acetonitrile/acetic acid was used as solvent the photolysate was kept over solid Na_2CO_3 for 24 h before being filtered and analyzed by GLC in the usual way.

Sensitized Reactions. The sensitization experiments were performed at 250 ± 8 nm with acetonitrile solutions of **2a** and triphenylene. The proportion of light absorbed by the components of the mixture was calculated from the integrated absorption over the bandwidth. Analysis was by GLC.

Quenching Experiments. The experiments were conducted at 306 ± 8 nm with acetonitrile solutions of **2a** and ferrocene or 3,3,4,4-tetramethyldiazetine *N,N'*-dioxide. The analysis was carried out by GLC. When [ferrocene] $> 1.1 \times 10^{-2}$ M GLC analysis was complicated by ferrocene interference, but no way to avoid this, e.g., by changing column or by using HPLC, was found.

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Registry No. 1a, 72844-82-7; **1b**, 72844-83-8; **1c**, 72844-84-9; **1d**, 72844-85-0; **1e**, 72844-86-1; **2a**, 72844-87-2; **2b**, 72844-87-2; **2c**, 72844-88-3; **2d**, 72844-89-4; **2e**, 72844-90-7; **3a**, 1721-89-7; **3c**, 1721-91-1; **3d**, 5278-43-3; **3e**, 72248-92-1; **3e** picrate, 72844-91-8; *o*-allylaniline, 32704-22-6; *o*-bromoacetanilide, 614-76-6; styrene, 100-42-5; *trans*-1-(*o*-nitrophenyl)prop-1-ene, 4036-19-5; acrylonitrile, 107-13-1; *o*-bromothioacetanilide, 62635-46-5.

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