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Photocycloaddition of Thiocarbonyl Compounds to Multiple Bonds. VII. The Reaction of Thiobenzophenone with Acetylenic Compounds

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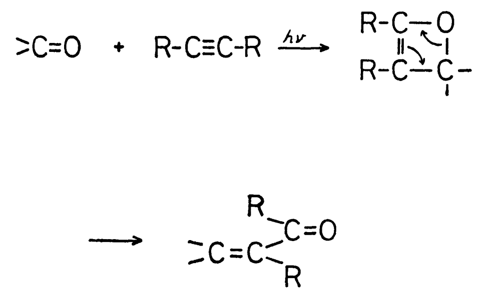
Photocycloaddition of thiobenzophenone to acetylenic compounds, R–C≡C–R′ (R=COOH, Ph, CH_2OH, and CN; R′=H: R=COOMe; R′=COOMe), affords 1-phenyl-2-thia-1,2-dihydronaphthalene derivatives. The key step to the product is an intra-molecular aromatic substitution of the composite vinylic biradical **13**. The difference in reactivity of acetylenic and olefinic compounds as well as that between thiobenzophenone and benzophenone are discussed. Ethoxyacetylene does not undergo the reaction. This is interpreted in terms of electronegativity of a radical center in **13**. It is found that cyanoacetylene reacts with butanethiyl radical in contrast to its olefin analog, acrylonitrile.

It has been reported that the photocycloaddition of thiobenzophenone to olefins leads to the formation of 1,4-dithiane derivatives or to thietane derivatives depending on the wavelength of light utilized and the structure of the olefin.[1,2] Similar reactions with ketones are well known and always result in the formation of oxetane derivative.[3,4]

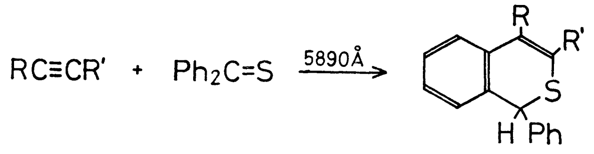
The Paterno-Büchi reaction is also applicable to acetylenic compounds. However, the oxetene derivatives formed are too unstable to be isolated and the final products are α,β-unsaturated ketones.[5,6] It is interesting to see whether the difference between ketones and thioketones observed in the reactions with olefins is also observed in the reactions with acetylenic compounds. Thus, we have studied the photocycloaddition of thiobenzophenone to several acetylene derivatives[7] and found that the reaction has completely different features from those involving olefins.



(1)

Results

The reactions of propiolic acid (**1**), phenylacetylene (**2**), propargyl alcohol (**3**), cyanoacetylene (**4**), and dimethyl acetylenedicarboxylate (**5**) yielded 1-pnenyl-2-thia-1,2-dihydro-4-naphthoic acid (**7**), 1,4-diphenyl-2-thia-1,2-dihydronaphthalene (**8**), 1-phenyl-2-thia-1,2-dihydro-4-hydroxymethylnaphthalene (**9**), 1-phenyl-2-thia-1,2-dihydro-4-cyanonaphthalene (**10**), and dimethyl 1-phenyl-2-thia-1,2-dihydronaphthalene-3,4-dicarboxylate (**11**), respectively, after irradiation with 5890 Å light from sodium lamps (480 W). The reaction with ethoxyacetylene (**6**) did not proceed under these conditions. Reaction conditions and yields of products are summarized in Table 1.



1—5	**7—11**
1; R=COOH, R′=H	**7**; R=COOH, R′=H
2; R=Ph, R′=H	**8**; R=Ph, R′=H
3; R=CH_2OH, R′=H	**9**; R=CH_2OH, R′=H
4; R=CN, R′=H	**10**; R=CN R′=H
5; R=COOMe, R′=COOMe	**11**; R=COOMe, R′=COOMe
6; R=OEt, R′=H	

The structures of the products were identified by NMR, IR, Mass spectra, elemental analyses, and chemical reactions. When **8** was treated with Raney Ni (W-2), it afforded 1,3-diphenylindane in 73% yield by reductive desulfuration.[8,9] The compound **9** was synthesized independently in 89% yield by reduction of **7** with lithium aluminum hydride. The carboxylic acid was also converted into **10** in several steps (27%).

When **8** was titrated with bromine in carbon tetrachloride, one equivalent of bromine was consumed and, after recrystallizations from ethanol, 1,4-diphenyl-2-thia-1,2-dihydro-3-ethoxynaphthalene (**12**) was isolated.

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[5] G. Büchi, J. T. Kofron, E. Loller, and D. Rosenthal, *J. Amer. Chem. Soc.*, **78**, 876 (1956).

[6] H. J. T. Bos and J. Boleiji, *Rec. Trav. Chim. Pays-Bas*, **88**, 465 (1969).

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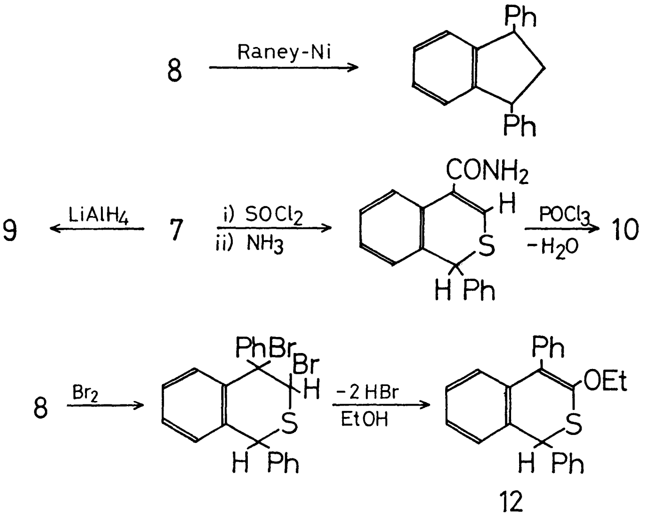
TABLE 1.[a] REACTIONS OF THIOBENZOPHENONE WITH ACETYLENES

Acetylene	Thiobenzophenone/ Acetylene, g/g	Solvent, ml	Reaction time, hr	Product	Yield,[b] %
1	2.5/10.0	THF, 40	240	**7**	26
2	3.0/12.0	Cyclohexane, 40	70	**8**	56
3	3.0/12.0	Cyclohexane, 40	115	**9**	28
4	2.5/10.0	Ether, 40	36	**10**	20
5	3.0/12.0	THF, 40	20	**11**	28
6	2.5/10.0	Cyclohexane, 40	500	no reaction	

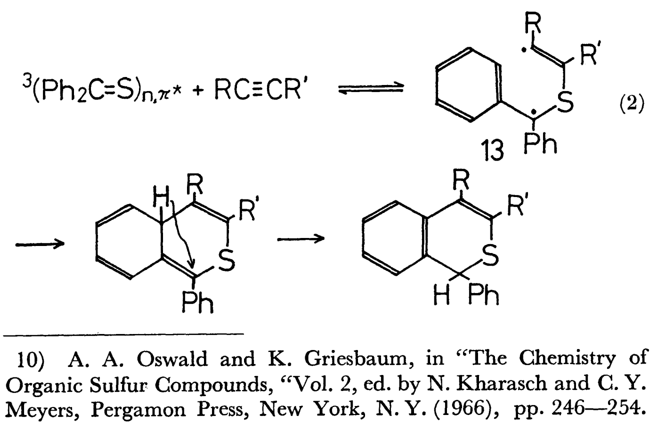
a) Reactions were carried out at the temperature of running water.
b) Based on thiobenzophenone.



Discussion

As previously reported,[1a] it is evident that irradiation with 5890 Å light excites thiobenzophenone to its n,π^* singlet state, which is rapidly deactivated to n,π^* triplet state by intersystem crossing. Since the n,π^* triplet state of thiobenzophenone behaves similarly to a thiyl radical,[1a] the reaction is undoubtedly initiated by the attack of the n,π^* triplet state of thiobenzophenone to an unsaturated carbon atom[10] and the following is the most reasonable mechanism:

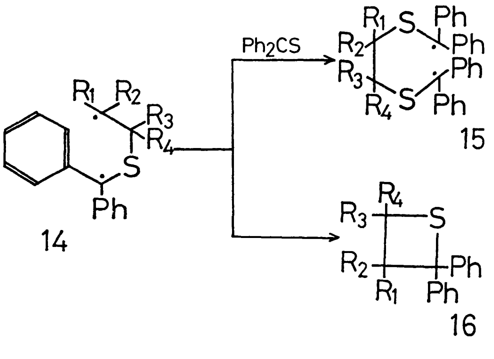
$$\mathrm{Ph_2C{=}S} \xrightarrow{5890\,\text{Å}} {}^{3}(\mathrm{Ph_2C{=}S})_{n,\pi^*}$$



(2)

The last step of the reaction, intra-molecular hydrogen migration, has been proved by the aid of deuterium-labelling technique. Thus, no deuterium was incorporated in the product even when the reaction was carried out in perdeuterated isopropyl alcohol or in deuterated chloroform as a solvent. However, since this is thermally forbidden 1,3-sigmatropic migration,[11] the actural course might be more complicated.

The above results exemplify the difference in reactivity of σ- and π-radicals. When an olefin is employed as a substrate, the radical center at the end carbon in the intermediate biradical **14**, where an odd electron exists in a p-orbital (π-radical), either attacks another molecule of thiobenzophenone forming another composite biradical **15**, or combines with the radical center at the benzhydryl position forming a stable molecule **16**. The reaction course depends on the nature of the R groups. It is known that the thiocarbonyl-sulfur is preferentially attacked by such carbon radicals.[12]



On the other hand, the corresponding radical center in **13** contains an odd electron in a sp^2 orbital (σ-radical) and can only attack the thiocarbonyl-sulfur with difficulty, which is in contrast to the facile attack on the aromatic ring.[13–15] Thus, the reactivity toward a phenyl ring and that toward a thiocarbonyl-sulfur are reversed in **13** and **14**. The fact that the reaction with **6** does not proceed, contrary to the expectation that the

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10) A. A. Oswald and K. Griesbaum, in "The Chemistry of Organic Sulfur Compounds, "Vol. 2, ed. by N. Kharasch and C. Y. Meyers, Pergamon Press, New York, N. Y. (1966), pp. 246—254.

11) J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," 3rd Ed., McGraw-Hill Book Co., New York, N. Y. N. Y. (1970), pp. 860—862.

12) G. Tsuchihashi, M. Yamauchi, and A. Ohno, This Bulletin, **43**, 968 (1970). The lower the ionization potential of a radical, the larger the tendency to attack thiobenzophenone.

addition of n,σ^* triplet state of thiobenzophenone to an electron-rich carbon-carbon triple bond might be fast,[1a, 16)] supports the interpretation. That is, an α-oxygen increases the inoization potential of an odd electron by its inductive effect. This reduces the facility of a radical to attack the aromatic ring. Since the electronegativity of an orbital of σ-radical that has an α-oxygen is not as small as that of a π-radical, it cannot attack the thiocarbonyl-sulfur either. Consequently, the thiobenzophenone is regenerated from **13** by the reverse reaction. It should be noted that all these reactions are competitive.

Although no concrete evidence has yet been obtained for a discussion of factors that result in combination of two radical centers in carbonyl compounds (Eq. (1)) and aromatic substitution in thiocarbonyl compounds (Eq. (2)), one possible explanation is that a longer bond length and smaller bond angle in the C–S–C moiety than in the C–O–C leads **13** to favorable cyclization over its oxygen analog.[17)] It should be noted that the attack to an aromatic ring must take place from the side of out-of-plane with the ring and the biradical should be helical.[18)] An alternative possibility is the n,π^* singlet state being the active species in the reaction of carbonyl compounds, where a four-membered ring is formed in one-step.[19)] We cannot expect a larger reactivity of the *ortho*-position in the thiobenzophenone moiety in **13** than that of its oxygen analog, because spin densities at *ortho*–positions in thiobenzophenone ketyl and in benzophenone ketyl are almost equivalent.[20)]

Herein arises another important difference between olefinic and acetylenic compounds. The potocycloaddition of thiobenzophenone to acrylonitrile and methyl acrylate proceeds *via* an ionic mechanism. Thus, only irradiation with 3660 Å light is effective, because this wavelength excites thiobenzophenone to its π,π^* singlet state, which has the character of a thiolate anion.[1a, c)] Irradiation with 5890 Å light, however, is ineffective in producing photocycloadducts with these olefins, because a thiyl radical-like species is produced in this process. In contrast, the corresponding acetylene analogs, **4** and **1**, undergo the reaction on irradiation with 5890 Å light. It is highly unlikely to expect the n,π^* singlet state of thiobenzophenone as reactive species in the reaction with acetylenes under the above conditions.[21)] Thus, we should expect that these acetylenic compounds react with the n,π^* triplet state of thiobenzophenone or a thiyl radical.

This difference can be interpreted in terms of molecular orbital considerations. Since an acetylenic bond is composed of two orthogonal π-orbitals, even if electrons in one orbital are withdrawn by an electron-attracting group, others in the second orbital will be rearranged to compensate the charge-separation in the molecule. Consequently the electron-deficiency at the end carbon is not as great as that in the corresponding position in olefinic compounds and this is still susceptible to the electrophilic attack of a thiyl radical. The situation is visualized in Figure 1 with **4**, where two molecular orbitals of π-symmetry ($\chi\pi_1$ and $\chi\pi_2$) are calculated by McLean and Yoshimine with SCF-LCAO-MO method with Slater–type functions.[22)]

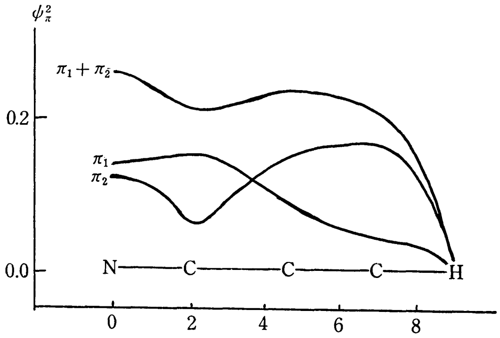

Fig. 1. A diagram for the π-electron densities in cyanoacetylene.

In order to test whether the above theoretical consideration is applicable to true thiyl radicals, we have studied radical additions of butanethiol to cyanoacetylene and found that cyanoacetylene *does* add the thiol, affording 2-(n-butylthio)acrylonitrile, under conditions where the reaction with acrylonitrile does not proceed,[23)] indicating larger susceptibility of cyanoacetylene than acrylonitrile to the attack of thiyl radicals. We do not, of course, consider this to be the only reason for the difference between acetylenic and olefinic compounds.

Experimental

Material. Thiobenzophenone was prepared and puri-

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14) a) A phenyl radical derived from phenylazotriphenylmethane cannot easily be captured by thiobenzophenone: G. Tsuchihashi and M. Yamauchi, personal communication, 1969; b) A styryl radical derived from cinnamoyl peroxide attacks a phenyl ring very easily, provided certain oxidizing agents are present: N. Wada, K. Tokumaru, and O. Simamura, personal communication, 1970; c) N. Wada, PhD Thesis, The Univ. of Tokyo, December 1970.

15) M. Levy and M. Szwarc, *J. Amer. Chem. Soc.*, **76**, 5981 (1954).

16) H. J. Alkema and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **79**, 1257 (1960).

17) Investigations with Driding models reveal that the end vinylic carbon in **13** can position itself over the carbon of a phenyl ring with only slight strain in the C-S-C angle, while the corresponding carbon in the oxygen analog of **13** of located far from the phenyl ring.

18) G. H. Williams, "Homolytic Aromatic Substituion," Pergamon Press, New York, N. Y. (1960), p. 50.

19) a) N. J. Turro, P. Wriede, J, C. Dalton, D. Arnold, and A. Grick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967); b) N, J. Turro and P. A. Wriede, *ibid.*, **90**, 6863 (1968); c) N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970); d) J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.*, **92**, 1318 (1970).

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23) C. D. Hurd L. L. Gershbein, *J. Amer. Chem. Soc.*, **69**, 2328 (1947).

fied as previously described.[24,25] Commercial acetylenes were used except for cyanoacetylene.[26] They were purified by distillation prior to use.

Photocycloaddition. The reaction was carried out in tetrahydrofuran, ether, or cyclohexane as an inert solvent. Isopropyl alcohol-d_8 and chloroform-d_1 were also inert to the reaction. The apparatus and detailed procedure have been described.[18a,25]

Characterization of 1-Phenyl-2-thia-1,2-dihydro-4-naphthoic Acid (7). After the reaction, the solvent was evaporated under reduced pressure. A mixture of ether and *n*-hexane was added to the residue, which was allowed to stand in a refrigerator until precipitation occurred. The crystals were filtered and the filtrate was subjected to silica gel column chromatography with *n*-hexane - chloroform (8:3) mixture as an eluent. Crystals thus obtained were combined to the former ones and recrystallized from aq-acetone giving 0.88 g (26% yield) of **7**: mp 164—166°C: NMR δ ($CDCl_3$, TMS); 5.13 (d, H, J=1.5 Hz), 7.90 (d, R′=H, J=1.5 Hz), 6.90—7.44 and 8.00—8.12 (m, H_{ar}), and 10.21 (s, CO_2H): IR; 3050, 3010, 1660, 1420, and 1260 cm^{-1}: MS *m/e* (species, %); 268 (M^+, 100), 250 (M^+-18, 10), 235 (M^+-SH, 14), 221 (M^+-HCO_2H, 24), 191 (M^+-Ph, 134), and 145 (PhC_2-HCO_2, 13): MW; Calcd for $C_{16}H_{12}O_2S$: 268. Found: 265.

Found: C, 71.61; H, 4.56; S, 11.94%. Calcd for $C_{16}H_{12}O_2S$: C, 71.64; H, 4.48; S, 11.94%.

Characterization of 1,4-Diphenyl-2-thia-1,2-dihydronaphthalene (8). The solvent was evaporated from a reaction mixture under reduced pressure. The residue was chromatographed on silica gel with *n*-hexane — chloroform (8:3) mixture as an eluent yielding 2.55 g (56% yield) of a pale green glassy solid, **8**. All attempts, for further purification including separation on tlc, were unsuccessful.[27] However, the structure was confirmed by chemical reactions as well as the following spectral data: NMR δ (CCl_4, TMS); 4.96 (d, H, J=1.0 Hz), 6.19 (d, R′=H, J=1.0 Hz), and 6.85—7.20 (m, H_{ar}): IR; 3050, 3010, 1600, and 1450 cm^{-1}: MS *m/e* (species, %): 300 (M^+, 100), 267 (M^+-SH, 27), 223 (M^+-Ph, 103), and 178 (PhC_2HPh, 10): MW; Calcd for $C_{21}H_{16}S$: 300. Found; 275.

Characterization of 1-Phenyl-2-thia-1,2-dihydro-4-hydroxymethylnaphthalene (9). The residue obtained from the usual treatment was chromatographed on silica gel. The chromatogram was developed by 300 m*l* of *n*-hexane — chloroform (4:6) mixture and was then eluted by chloroform yielding 1.08 g (28% yield) of pale yellow oil, **9**. This compound is highly hygroscopic.[27] The structure was confirmed by chemical and spectral evidence: NMR δ ($CDCl_3$, TMS); 2.90 (broad s, OH), 4.51 (Broad s, CH_2), 5.05 (d, H, $J<0.5$ Hz), 6.36 (d, R′=H, $J<0.5$ Hz), and 6.90—7.54 (m, H_{ar}): IR 3500—3100, 3040—3000, 765, and 695 cm^{-1}: MS *m/e* (species, %); 254 (M^+, 100), 221 (M^+-SH, 20), 177 (M^+-Ph, 156), and 115 (PhC_3H_3, 34).

Characterization of 1-Phenyl-2-thia-1,2-dihydro-4-cyanonaphthalene (10). The residue obtained was chromatographed on silica gel with *n*-hexane — chloroform (9:1) mixture as an eluent. The solid thus obtained was recrystallized from aq-ethanol yielding 0.615 g (20% yield) of **10**: mp 70—72°C: NMR δ ($CDCl_3$, TMS); 5.21 (d, H, $J<0.5$ Hz), 7.10 (d, $J<0.5$ Hz),[28] and 6.80—7.85 (m, H_{ar}): IR; 3080—3000, 2217, 1580, 1540, and 1440 cm^{-1}: MS *m/e* (species, %); 249 (M^+, 100), 222 (M^+-HCN, 8), 216 (M^+-SH, 12), and 172 (M^+-Ph, 172).

Found: C, 76.85; H, 4.74; N, 5.53; S, 12.88%. Calcd for $C_{16}H_{11}NS$: C, 77.07; H, 4.45; N, 5.62; S, 12.86%.

Characterization of Dimethyl 1-Phenyl-2-thio-1,2-dihydronaphthalene-3,4-dicarboxylate (11). The residue obtained was chromatographed on silica gel with *n*-hexane - chloroform (8:3) as an eluent. Crystals thus obtained were recrystallized from *n*-hexane - benzene mixture, yiedling 1.45 g (28.3% yield) of **11**; mp 90—91°C: NMR δ (CCl_4, TMS); 3.66 (s, CH_3), 3.80 (s, CH_3), 5.05 (s, H), 6.78—6.94 and 7.02—7.50 (m, H_{ar}): IR; 1710—1745 cm^{-1} ($\nu_{C=O}$): MS *m/e* (species, %); 340 (M^+, 100), 309 (M^+-OCH_3, 22), 307 (M^+-SH, 9), 263 (M^+-Ph, 170), and 221 ($PhC_6H_4\cdot C_2S$, 98).

Found: C, 67.08; H, 4.96; S, 9.42%. Calcd for $C_{19}H_{16}O_4S$: C, 67.04; H, 4.74; S, 9.42%.

Reductive Desulfuration of 8. A mixture of 0.73 g of **8** and excess Raney Ni (W-2) in benzene was refluxed for 27hr. After the reaction, the mixture was filtered and the solvent was evaporated from the filtrate under reduced pressure. The remaining crystals were recrystallized from benzene-methanol (1:1) mixture giving 0.48 g (73% yield) of 1,3-diphenylindane: mp 157—159°C (lit,[29] 156—157°C). The spectral data also supported the structure.

Bromination of 8. An ice-cooled carbon tetrachloride (3 m*l*) solution of **8** (4.33×10^{-4} mol) was titrated with 6.25×10^{-2}N solution of bromine in carbon tetrachloride. The bromine was consumed when 7 m*l* of the solution (4.375×10^{-4} mol of Br_2) had been added. The mixture was stirred for additional 1 hr. A small amount of precipitate thus obtained was filtered and recrystallized from ethanol. The structure of the crystal was identified by NMR and mass spectra to **12**: NMR δ (DMSO-d_6, TMS); 1.12 (t, 3H), 3.43 (q, 2H), 6.78 (s, 1H), and 7.40 (m, 14H): MS *m/e* (species, %); 344 (M^+, 100), 300 (M^+-CH_3CHO, 422), 267 (M^+-Ph and/or 300-SH, 56), 223 (300-Ph, 81), and 165 ($PhC\cdot C_6H_4$, 69).

Reduction of 7 to 9.[30] Into a three-necked flask containing 47 mg of $LiAlH_4$ and 5 m*l* of dry ether, 263 mg of **7** in 20 m*l* of dry ether was added slowly with stirring. The mixture was stirred for 10 hr under refluxing. Ethanol, water, and 10% H_2SO_4 were then added successively to decompose excess $LiAlH_4$. The organic materials were extracted with ether and the ether layer was dried over Drierite. After the solvent was evaporated under reduced pressure, 0.221 g (89% yield) of pale yellow oil remained, whose NMR, IR, and mass spectra were identical with those of **9** obtained by photocycloaddition.

Conversion of 7 to 10.[31,32] A mixture of **7** (0.968 g) and $SOCl_2$ (1.0 g) was kept at 30—35°C for 3 hr. The mixture was cooled in an ice-bath and 30 m*l* of conc. NH_4OH was added dropwise. The organic materials were extracted with chloroform and the chloroform layer was dried over Drierite. Crude crystals of the amide (0.35 g) were obtained after evaporation of the solvent under reduced pressure: mp 145—149°C: NMR δ ($CDCl_3$, TMS); 5.15 (d, 1H, $J<0.5$ Hz), 5.94 (broad

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[26] We thank Dr. K. Morita of Takeda Chemical Industries, Ltd. for kindly supplying this compound.

[27] Elemental analyses had a deviation of about 1% from the theoretical value for carbon, although satisfactory results were obtained for sulfur.

[28] Identified by spin decoupling technique.

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[32] A. R. Surrey, *ibid.*, Coll. Vol. III, p. 535 (1955).

s, 2H), and 7.10—7.50 (m, 10H): IR; 3990, 3190, 1640, 1613, 1485, and 1414 cm^{-1}.

To a mixture of the amide (0.35 g), NaCl (1.5 g), and CCl_4 (10 m*l*) ,0.3 g of $POCl_3$ was added with stirring, and the mixture was refluxed for 3 hr. The mixture was cooled to room temperature. The precipitate was filtered and the filtrate was dried over Drierite. After evaporation of the solvent under reduced pressure, 0.23 g (27% yield based on **7**) of **10** was obtained: mp 70—72°C. Spectral data were identical with those of **10** obtained by photocycloaddition.

Photoaddition of n-*Butanethiol to 4.*　A mixture of *n*-butanethiol (1.76 g) and **4** (1.0 g) was prepared in a dry box under an atmosphere of CO_2. To a half portion of this mixture was added 50 mg of benzoylperoxide (BPO). The two half portions were placed in Vycor ampules. The ampules were vacuum-sealed and subjected to irradiation with light of 2537 Å from a 160 W low-pressure mercury lamp (Riko-Kagaku Sangyo) for 3 hr at room temperature. The oily products obtained after evaporating volatile materials were chromatographed on silica gel with *n*-hexane containing 10% benzene as an eluent. The products were identified to be *cis*-2-(*n*-butylthio)acrylonitrile, contaminated by a small amount of the *trans*-isomer, by the following evidence: NMR δ (CCl_4, TMS); 0.95 (m, 3H), 1.57 (m, 4H), 2.90 (t, 2H, J= 6.8 Hz), 5.22 (d, 1H, J=10.5 Hz), and 7.11 (d, 1H, J=10.5 Hz).

Yields were determined by vpc (Hitachi K-53 (FID) with a column of 20% SE-30 at 150°C) to be 13.7% (without BPO) and 27.0% (with BPO).

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