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Photochemical Reactions of Some Thiocarbonyl Trimers

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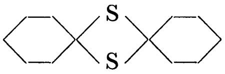
Although the photochemical reactions of diaryl thiocarbonyls have been extensively studied,[1] those of dialkyl or alkyl-aryl thiocarbonyls have not yet been given attention. Generally, monomeric dialkyl or alkyl-aryl thiocarbonyls are unstable and readily trimerize at room temperature. Previously, we reported the photochemical formation of a monomeric thiocarbonyl from the corresponding trimer.[2] In this paper we want to report that the irradiation of some thiocarbonyl trimers give a thiophene, a dithietane, and/or a disulfide.

When the thioacetophenone trimer (**1**) in cyclohexane was irradiated, the solution turned blue (λ_{max} 575 nm),[3] showing the formation of thioacetophenone (**7**). After irradiation for 2 hr, the product was treated with cyclopentadiene to give an 1:1-adduct (**8**) of **7** and cyclopentadiene. The NMR spectrum of **8** showed two singlets, at τ 8.49 and 8.39 and in a ratio of 1.9: 1.1, assignable to methyl protons at C-3. The product, **8**, was therefore considered to be a mixture of *endo*- and *exo*-isomers. The prolonged irradiation (24 hr) of **1** gave 2,4-diphenylthiophene (**9**) (15%), 9,10-dimethylphenanthrene (**10**) (8%), and an unidentified product (**11**) (3.75%), which was then converted into **9** by distillation (175—178 °C/2 mmHg). The structure of **9** was established on the basis of the results of elemental analysis and the spectral data by comparison with an authentic sample.[4] The formation of **10** seems to proceed through the cyclization of dimethylstilbene,[5] which is photochemically derived from **7**, whlie thiobenzophenone gives tetraphenylethylene on irradiation.[1a)]

The irradiation of the thiobenzaldehyde trimer (**2**) in dioxane gave *cis*-stilbene (**12**), *trans*-stilbene (**13**) (combined yield, 3.5%), and phenanthrene (**14**) (3.5%). Compounds **12** and **13** may be derived from a thiobenzaldehyde monomer like **1** and are presumed to be precursors of **14**.[5]

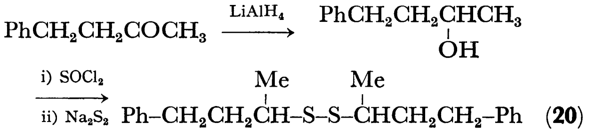
The irradiation of the cyclohexanethione trimer (**3**) in cyclohexane yielded 7,14-dithiadispiro[5.1.5.1]-tetradecane (**15**) (20%) and dicyclohexyl disulfide (**16**) (10%). The formation of **15** is presumed to proceed through the dimerization of cyclohexanethione, formed from **3** by light, because on irradiation the solution of **3** immediately turns pink (λ_{max} 504 nm),[6] showing the formation of cyclohexanethione. On the other hand, Compound **16** probably arises from **15**, since Berchtold *et al.*[7] reported that the photolysis of 1,4-dithiaspiro[4.5]decane afforded **15** and was followed by the formation of **16**.



(**15**)

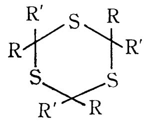
The irradiation of the thioacetone trimer (**4**) in cyclohexane yielded 2,2,4,4-tetramethyl-1,3-dithietane (**17**) (35%) and diisopropyl disulfide (**18**) (21%). These photoproducts undoubtedly arise from the thioacetone monomer, which may be formed by an initial C–S bond cleavage of **4**.

The irradiation of other thiocarbonyl trimers (**5**) and (**6**) gave the corresponding disulfides, (**19**) (15%) and (**20**) (20%) respectively. The disulfide **20** was confirmed by unequivocal synthesis from benzylacetone.

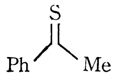


$$PhCH_2CH_2COCH_3 \xrightarrow{LiAlH_4} PhCH_2CH_2\underset{\substack{|\\ OH}}{C}HCH_3$$

$$\xrightarrow[\text{ii) }Na_2S_2]{\text{i) }SOCl_2} Ph\text{–}CH_2CH_2\overset{\substack{Me\\ |}}{C}H\text{–}S\text{–}S\text{–}\overset{\substack{Me\\ |}}{C}HCH_2CH_2\text{–}Ph \quad (\mathbf{20})$$



1 R=Ph R'=Me
2 R=Ph R'=H
3 R=R'=–$(CH_2)_5$–
4 R=R'=Me
5 R=$PhCH_2$ R'=H
6 R=$PhCH_2CH_2$ R'=Me



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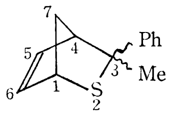

8

Experimental

Materials. The thiocarbonyl trimers, **1**, **2**, **4**, and **5**, were prepared according to previouly-proposed procedures.[8-11] **3** was synthesized by modifying the method of Baumann;[8] mp 99—100 °C (lit,[12] 102 °C).

2,4,6-Triphenethyl-2,4,6-trimethyl-1,3,5-trithiane (6). Dry HCl was bubbled through a solution of 25 g of benzylacetone in 250 ml of ethanol with stirring below 0 °C for

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30 min. Then H_2S was passed through until precipitation formation came to the end. The precipitates were collected by filtration and were recrystallized from acetone to give 10 g of **6**; mp 130—131 °C. IR: $\nu_{\max}^{\text{KBr}}$ cm^{-1}, 3020, 1600, 1490, 1365, 753, 730, 700. NMR: (τ in $CDCl_3$) 8.17 (s, 9H, $3\times$Me), 7.86—6.92 (A_2B_2 m, 12H, $6\times CH_2$), 3.10—2.63 (m, 15H, $3\times$Ph). Found: C, 73.25; H, 7.51%. Calcd for $C_{30}H_{36}S_3$: C, 73.14; H, 7.37%.

Irradiation of 1. (a) When a solution of 1 g of **1** in 150 ml of cyclohexane was irradiated with a low-pressure mercury lamp in a quartz tube under nitrogen, the blue color of **7** gradually appeared with time. After irradiation for 2 hr, 1 g of cyclopentadiene was added to the reaction mixture and it was stirred until the blue color disappeared at room temperature. After the removal of the solvent, the residue was chromatographed on a silica-gel column. Elution with *n*-hexane–benzene(9: 1) gave 100 mg of 3-phenyl-3-methyl-2-thianorbornene (**8**); IR: $\nu_{\max}^{\text{film}}$ cm^{-1}, 3050, 1598, 1575, 1490, 765, 748, 702. NMR: (τ in $CDCl_3$) 8.49 (s, 1.9H, *endo*-Me) and 8.39 (s, 1.1H, *exo*-Me), 8.11 (m, 2H, CH_2), 6.63 and 6.03 (m, 2H, $2\times$CH), 3.90 and 3.68 (m, 2H, vinyl), 3.05—2.2 (m, 5H, Ph). Found: C, 77.24; H, 6.60%. Calcd for $C_{13}H_{14}S$: C, 77.20; H, 6.98%.

(b) A solution of 1 g of **1** in 150 ml of cyclohexane was irradiated for 24 hr. After the removal of the solvent, the residue was chromatographed on a silica gel column with *n*-hexane–benzene (19: 1) to give 150 mg of **9**, 80 mg of **10**, and 37.5 mg of **11**.

(i) 2,4-Diphenylthiophene (**9**); mp 118.5—120.5 °C (lit,[13] 121.0—121.5 °C). UV: $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε), 223.5 (sh. 19900), 256 (54200), 301 (sh. 11400).

(ii) 9,10-Dimethylphenanthrene (**10**); mp 138—139 °C (lit,[14] 139 °C). NMR: (τ in $CDCl_3$) 8.30 (s, 6H, $2\times$Me), 2.58—2.30 (m, 4H, aromatic), 2.06—1.78 (m, 2H, aromatic), 1.48—1.20 (m, 2H, aromatic).

Irradiation of 2. A solution of 1 g of **2** in 150 ml of dioxane was irradiated for 15 hr. After the removal of the solvent, the residue was chromatographed on a silica gel column with *n*-hexane–benzene (9: 1) to give 15 mg of **12**, 20 mg of **13**, and 35 mg of **14**. Each product was identified with the corresponding authentic sample by comparing the spectral data.

Irradiation of 3. A solution of 1 g of **3** in 150 ml of cyclohexane was irradiated for 15 hr. After the removal of the solvent, the residue was chromatographed on a silica gel column with *n*-hexane–benzene (9: 1) to give 200 mg of **15**, 100 mg of **16**, and 150 mg of unchanged **3**.

(i) 7,14-Dithiadispiro[5.1.5.1]tetradecane (**15**); Recrystallizations from *n*-hexane afforded prisms; mp 131—132 °C (lit,[15] 132—133 °C). NMR: (τ in $CDCl_3$) 9.0—8.18 (m, 12H, $6\times CH_2$), 8.18—7.62 (m, 8H, $4\times CH_2$). Mass spectrum: *m/e*, 228 (M^+), 114 ($M-C_6H_{10}S$) and 81.

(ii) Dicyclohexyl disulfide (**16**); bp 125—128 °C/4—5 mmHg (lit,[7,17] 98 °C/2 mmHg, 100 °C/0.01 mmHg). NMR: (τ in $CDCl_3$) 9.40—7.40 (m, 20H, $10\times CH_2$), 7.30 (br s, 2H, $2\times$CH). Mass spectrum: *m/e*, 230 (M^+), 148 ($M-C_6H_{10}$), 115 ($M-C_6H_{11}S$) and 83.

Irradiation of 4. A solution of 1 g of **4** in 150 ml of cyclohexane was irradiated for 20 hr. After the removal of the solvent, the residue was chromatographed on a silica gel column with *n*-hexane–benzene (9: 1) to give 350 mg of **17** and 210 mg of **18**.

(i) 2,2,4,4-Tetramethyl-1,3-dithietane (**17**). Recrystallization from *n*-hexane afforded needles; mp 77—78 °C (lit,[16] 77—77.5 °C). UV: $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε), 233.5 (180), 303.5 (20). Mass spectrum: *m/e*, 148 (M^+), 74 ($M-C_3H_6S$) and 59.

(ii) Diisopropyl disulfide (**18**); bp 72—75 °C/20 mmHg (lit,[17] 70 °C/20 mmHg). IR: $\nu_{\max}^{\text{film}}$ cm^{-1}, 1380, 1368. NMR: (τ in $CDCl_3$) 8.70 (d, 12H, $4\times$Me), 7.01 (sep, 2H, $2\times$CH). Mass spectrum: *m/e*, 150 (M^+), 107 ($M-C_3H_7$), 75 ($M-C_3H_7S$) and 59.

Irradiation of 5. A solution of 1 g of **5** in 150 ml of tetrahydrofuran was irradiated for 20 hr. After the removal of the solvent, the residual oil was chromatographed on a silica gel column with *n*-hexane–benzene (4: 1) to give 150 mg of diphenethyl disulfide (**19**); bp 159—161 °C/4—5 mmHg (lit,[18] 150—155 °C/1 mmHg. NMR: (τ in $CDCl_3$) 7.05 (s, 8H, $4\times CH_2$), 2.77 (s, 10H, $2\times$Ph). Mass spectrum: *m/e*, 274 (M^+), 169 ($M-C_6H_5CH_2CH_2$), 137 ($M-C_6H_5CH_2CH_2S$), 105 ($M-C_6H_5CH_2CH_2SS$) and 91.

Irradiation of 6. A solution of 1 g of **6** in 150 ml of cyclohexane was irradiated for 15 hr. After the removal of the solvent, the residual oil was chromatographed on a silica gel column with *n*-hexane–benzene (4: 1) to give 200 mg of (1,1′-dimethyl-3,3′-diphenyl)dipropyl disulfide (**20**); bp 185—187 °C/4—5 mmHg. IR: $\nu_{\max}^{\text{film}}$ cm^{-1}, 3030, 2924, 2855, 1605, 1490, 1370, 750, 700. NMR: (τ in $CDCl_3$) 8.67 (d, 6H, $2\times$Me), 8.42—7.75 (m, 4H, $2\times CH_2$), 7.27 (t, 4H, $2\times CH_2$), 7.20 (m, 2H, $2\times$CH), 2.77 (s, 10H, $2\times$Ph). Mass spectrum: *m/e*, 330 (M^+), 197 ($M-C_6H_5CH_2CH_2C(Me)H$), 166 ($M-C_6H_5CH_2CH_2C({=}S)Me$), 165 ($M-C_6H_5CH_2CH_2CH(Me)S$), 132 ($M-C_6H_5CH_2CH_2CH(Me)SSH$). Found: C, 72.08; H, 7.99%. Calcd for $C_{20}H_{26}S_2$: C, 72.67; H, 7.90%.

Synthesis of **20** *from Benzylacetone.* To a solution of 1 g of $LiAlH_4$ in 30 ml of ether, a solution of 5 g of benzylacetone in 30 ml of ether was added. The solution was refluxed for 20 hr, poured into ice water, and then extracted with ether. The extract was dried over anhydrous Na_2SO_4 and evaporated to leave 4-phenylbutan-2-ol (5 g). The crude alcohol (5 g) was dissolved in 30 ml of DMF, and then thionyl chloride (5 g) was stirred in drop by drop. The whole was stirred for 12 hr, poured into ice water, and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated. The solution of the crude product (5 g) in 10 ml of alcohol was stirred into a solution of Na_2S_2 (from Na_2S-$9H_2O$ (5 g), S (0.6 g), and H_2O (5 ml)). The whole was then heated to 60 °C, stirred at that temperature for 7 hr, and extracted with *n*-hexane. The extract was then dried and evaporated. When the residual oil was chromatographed on a silica gel column with *n*-hexane–benzene (4: 1), it gave an oil which was subsequently distilled (bp 185—187 °C/4—5 mmHg) and found to be identical with the photoproduct (IR and NMR spectra and tlc) (2.5 g).

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