The Photochemistry of Aromatic Thiol Esters

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The photolysis of a variety of aromatic thiol esters was investigated in cyclohexane using a 254-nm light source. The photochemical reaction proceeds initially by cleavage of the *S*-acyl bond, giving rise to the corresponding aromatic thiyl radical and an acyl radical which sometimes decarbonylates. The resulting radicals recombine to give disulfides, sulfides, and hydrocarbons. Acyl radicals which are less prone to decarbonylation abstract hydrogen to form aldehydes. No photo-Fries rearrangement and a minor amount of Norrish type II cleavage were observed. Sulfide formation appears to be intermolecular.

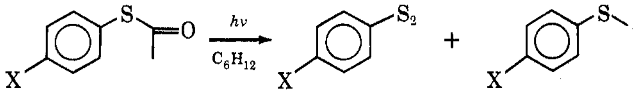
We found that the photolysis of 4-tolyl thiolacetate gave 4-tolyl disulfide and methyl 4-tolyl sulfide but no 4-toluenethiol nor any photo-Fries rearrangement.[2] Subsequently, Bradshaw and coworkers[3] reported the major products of the photolysis of phenyl thiolacetate to be phenyl disulfide, methyl phenyl sulfide, and thiophenol, which arises from secondary photolysis of phenyl disulfide without the intervention of solvent,[4] plus minor amounts of the corresponding photo-Fries products.

The purpose of this paper is to report the photochemistry of several aryl thiol esters in an effort to uncover partially the nature of the excited state responsible for the photoreaction, to discover whether or not sulfide formation is intramolecular, and to explain the lack of photo-Fries rearrangement in thiol esters.

Results

Irradiation of approximately 1% solutions of 4-substituted phenyl thiolacetates **1** in cyclohexane for 3 hr using a 254-nm light source produced the corresponding diphenyl disulfides **2** and methyl phenyl sulfides **3** as shown in Scheme I. In no case were the 4-substituted thiophenol or the photo-Fries rearrangement products found, a result which is in striking contrast to the reported photolysis of phenyl thiolacetate.[3] While esters **1a** and **1b** were 75 and 78% photolyzed after 3 hr, the nitro ester **1c** was only 47% gone because precipitation of the disulfide **2c** coated the vessel wall.

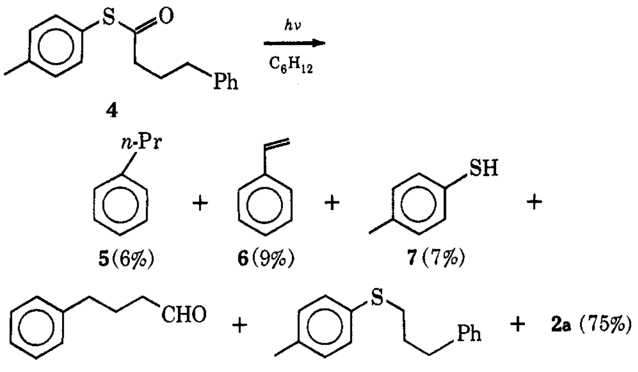
Scheme I



1a, X = CH_3 **2a**, 77% **3a**, 7%
b, X = $(CH_3)_2N$ **b**, 77% **b**, 7%
c, X = NO_2 **c**, 90% **c**, 8%

Irradiation of 4′-tolyl thiol-4-phenylbutyrate (**4**) with 254-nm light in cyclohexane solution (Scheme II) gave propylbenzene (**5**), styrene (**6**), 4-toluenethiol (**7**), 4-phenylbutanal (**8**), 3-phenylpropyl 4′-tolyl sulfide (**9**), 4-tolyl disulfide (**2a**), and a trace of 4-tolyl thiolacetate (**1a**). Clearly, the Norrish type II reaction is relatively inefficient as compared to cleavage of the *S*-acyl bond.

Scheme II



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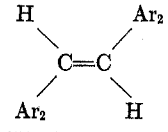
5 (6%) **6** (9%) **7** (7%)

8 (36%) **9** (2%) **2a** (75%)

To determine whether or not sulfide formation is intramolecular, photolysis of the esters phenyl 4-toluenethiolacetate (**10**) and 4′-tolyl benzenethiolacetate (**11**) was examined (Table I) because the expected acyl radicals readily decarbonylate. The photolysis of **10** gave 1,2-diphenylethane (**12**), benzyl 4-tolyl sulfide (**13**), and the disulfide **2a**. Thiol ester **11** formed not only 1,2-di(4′-tolyl)ethane (**14**), 4-tolyl phenyl sulfide (**15**), and diphenyl disulfide (**16**), but also 4-xylene (**17**), thiophenol (**18**), and *trans*-4,4′-dimethylstilbene (**19**). After 3 hr the esters **10** and **11** have photolyzed 85 and 87%, respectively. However, when an equimolar solution of **10** and **11** was photolyzed for

Table I[a]

Product Yields for hν of Esters 10 and 11

Products		hν of $Ar_1SC(=O)CH_2Ar_2$	hν of $Ar_2SC(=O)CH_2Ar_1$	hν of **10** + **11**
$(Ar_1CH_2)_2$	**12**		28	6
$(Ar_2CH_2)_2$	**14**	18		3
$Ar_1CH_2CH_2Ar_2$	**22**			2
$(Ar_1S)_2$	**16**	25		16
$(Ar_2S)_2$	**2a**		35	40
Ar_1SSAr_2	**23**			5
$Ar_1CH_2SAr_2$	**13**		13	5
$Ar_2CH_2SAr_1$	**15**	3		2
$Ar_1CH_2SAr_1$	**20**			6
$Ar_2CH_2SAr_2$	**21**			11
Ar_2CH_3	**17**	8		
Ar_1SH	**18**	18		
	**19**	19		

[a] Yields are given in per cent; $Ar_1 = C_6H_5$; $Ar_2 = 4\text{-}CH_3C_6H_4$.

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[1] Summer Faculty Research Fellow, Miami University, 1971.

[2] J. R. Grunwell, *Chem. Commun.*, 1437 (1969).

[3] E. L. Loveridge, B. R. Beck, and J. S. Bradshaw, *J. Org. Chem.*, **36**, 221 (1971).

[4] Y. Schoafsma, A. F. Bickel, and E. Y. Kooyman, *Tetrahedron*, **10**, 76 (1960).

3 hr in cyclohexane, **10** disappeared about twice as fast as **11**. In addition to products **12–16**, the mixed sulfides **20** and **21**, the mixed hydrocarbon **22**, and the mixed disulfide **23** were also formed. Sulfide formation appears to be intermolecular for these esters. Laarhoven and coworkers have shown that benzyl sulfides photodissociate to benzyl and thiyl radicals.[5a,b] However, this reaction is slower than the photodissociation of the thiol esters. For instance, the sulfide **15** disappeared 40% after 3 hr of photolysis under identical conditions as **10** and **11**.[5c] Therefore, the "cross" sulfides arise only partially from secondary photolysis of **13** and **15**. The product ratios for the photolysis of **10** and **11** are shown in Table II and are all between 2 and 2.5, while the ratio **10**/**11** = 2.22 for the disappearance of **10** and **11**.

TABLE II
PRODUCT RATIOS

Product	Ratio
10/**11**	2.22
12/**14**	2.00
2a/**16**	2.48
13/**15**	2.50
21/**20**	1.88

Another series of experiments which has bearing on the intramolecularity of sulfide formation is summarized in Table III. When 4-tolyl thiolacetate (**1a**) and an equimolar amount of thiophenol (**18**) dissolved in cyclohexane were photolyzed for 3 hr, phenyl thiolacetate (**24**), methyl phenyl sulfide (**25**), and 4-tolenethiol (**7**) in addition to the disulfides **16**, **2a**, and **23** were formed. Unfortunately, we were unable to observe the photo-Fries products.

TABLE III[a]
PHOTOLYSIS OF ARYLTHIOL ESTER WITH ARYLTHIOL

Compd		$Ar_1SC(=O)CH_3$ **1a** + Ar_1SH **18**	$Ar_1SC(=O)CH_3$ **24** + Ar_2SH **7**
Ar_1SH	**18**	4	8
Ar_2SH	**7**	5	6
Ar_1SCOCH_3	**24**	3	28
Ar_2SCOCH_3	**1a**	9	11
Ar_1SCH_3	**25**	5	0
Ar_2SCH_3	**3a**	<1	0
$(Ar_1S)_2$	**16**	32	4
$(Ar_2S)_2$	**2a**	14	22
Ar_1SSAr_2	**23**	16	9
Ar_1S-c-C_6H_{11}	**27**	2	<1
Ar_2S-c-C_6H_{11}	**26**	1	2

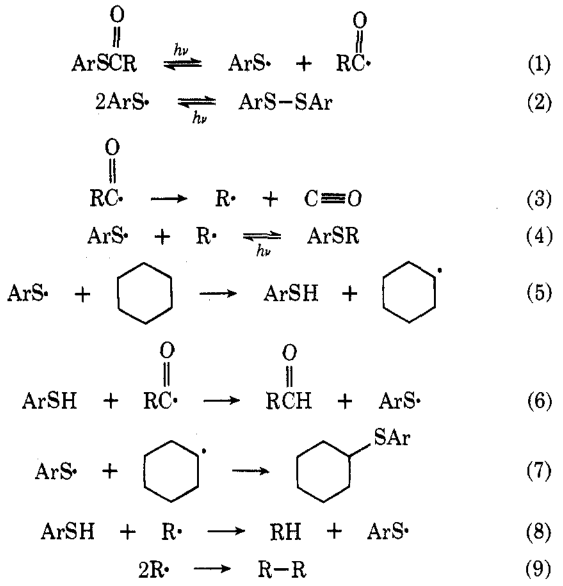
[a] Yields are given in per cent; $Ar_1 = C_6H_5$; $Ar_2 = 4\text{-}CH_3C_6H_4$.

When phenyl thiolacetate (**24**) and 4-toluenethiol (**7**) were photolyzed, the ester **1a** was formed in addition to the other products with the exception of the sulfides **3a** and **25**. The formation of methyl phenyl sulfide (**25**) from **1a** and **18** does not arise from secondary photolysis of **24**, since we found more **25** than **24**, and at no time does the sulfide **25** exceed the amount of ester **24** when **24** is irradiated in the absence of the thiol **7**, as shown by Bradshaw.[8] Therefore, sulfide formation appears to be intermolecular. Further, the acetyl radical has sufficient stability and lifetime to diffuse away from its original partner and then combine with another thiyl radical to generate a new ester. It seems possible that the photo-Fries rearrangement observed by Bradshaw may be intermolecular.

Discussion

The products of the photolyses seem best accounted for by homolytic cleavage of the S–acyl bond of the excited thiol ester followed by a series of dark reactions typical of the radicals produced. The proposed mechanism is summarized in Scheme III. The acyl radical is reduced to the corresponding aldehyde but will decarbonylate when the resulting radical is stabilized by a phenyl group. The acyl radical also reacts with the thiyl radical chiefly at sulfur, since the spin density of an aryl thiyl radical is largely localized on sulfur according to esr measurements.[6]

SCHEME III



The observed Norrish II cleavage[7] is inefficient as compared to the α cleavage of the S–acyl bonds. There is much less 4-tolyl thiolacetate than styrene. Two explanations are possible: (1) the concentration of the ester **1a** is reduced by secondary photolysis; or (2) most of the styrene is formed from a Norrish II cleavage of the phenylaldehyde **8**. The first hypothesis is unlikely, since the sulfide **3a** is not found. The second explanation seems plausible, since aldehydes are known to undergo Norrish II cleavage.[7] The inefficient Norrish II reaction of the phenylthiobutyrate ester **4** is mirrored by the lack of the corresponding McLafferty rearrangement in the mass spectrum of **4**.

The lack of a photo-Fries rearrangement for 4-substituted phenyl thiyl radicals is not strictly due to localization of spin on sulfur, since phenyl thiyl radical gives some photo-Fries products. Electron-donating and -withdrawing substituents will stabilize benzyl

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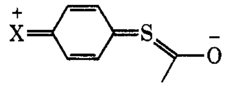
[7] P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

radicals by delocalization, and therefore it seems probable that what spin density is localized on the ortho position is diminished by the para substituent, thus rendering the ortho position of the thiyl radical unreactive.

While it seems likely that the photo-Fries rearrangement occurs by a radical mechanism,[8] the possibility exists that rearrangement proceeds through an intimate contact 1,3-sigmatropic change of order;[9] *i.e.*, the acyl group remains bonded to the rest of the molecule during rearrangement. If structures of the quinoid type such as **28** were important in the excited state



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of 4-substituted (electron-donating substituents) as proposed by Cilento[10] and Baliah,[11] then the photo-Fries rearrangement would be hindered, since the phenyl and acyl groups would be coplanar. However, we can find no evidence which establishes the importance of **28** in the excited state of phenyl thiolacetates.[12] Therefore we prefer the explanation based on a free-radical mechanism.

Experimental Section

Boiling and melting points are uncorrected. All uv spectra were recorded on a Cary 14 spectrophotometer, ir spectra on a Perkin-Elmer 237 spectrophotometer, nmr spectra on a Jeolco C-60H spectrometer, and mass spectra on a Hitachi RMU-6 spectrometer. Gas chromatograms were obtained from a Hewlett-Packard 700 chromatograph equipped with a 4-ft 10% Carbowax 20M (Chromosorb P), a 6-ft 10% Carbowax 20M (Chromosorb W), or a 6-ft 15% SE-30 (Chromosorb P) column. Microanalyses were performed by Galbraith Laboratories, Inc. Cyclohexane was purified by washing with 18 *N* sulfuric acid and then distilled water followed by distillation from barium oxide. Acetonitrile and 1,4-dioxane were Matheson spectroquality reagents. All photolysis experiments were conducted in a Rayonet photochemical reactor equipped with 2537-Å mercury vapor lamps. All photochemical yields are based on the amount of ester which has disappeared.

4-Tolyl Thiolacetate (1a).—From acetyl chloride, 70.0 g (0.90 mol), 107.0 g (0.86 mol) of 4-toluenethiol, and 110.0 g of triethylamine, there was obtained 120.0 g (85%) of **1a**: bp 122° (10 mm) [lit.[13] bp 120° (11 mm)]; ir (neat) 3490 (w), 3020 (w), 2910 (w), 2860 (w), 1710 (s), 1590 (w), 1490 (w), 1350 (m), 1120 (s), 1090 (m), 1020 (m), 950 (m), and 910 cm^{-1} (s); uv max (cyclohexane) 233 mμ (ε 12,000); mass spectrum (80 eV) *m/e* (rel intensity) 166 (3), 124 (61), 123 (21), 91 (32), and 43 (100).

Photolysis of 1a.—Oxygen was removed from a solution of 3.0 g (0.0018 mol) of **1a** in 600 ml of cyclohexane by bubbling dry prepurified N_2 gas into the solution, which was irradiated for 10 hr and evaporated to give 2.39 g of a residue which was a mixture of **1a**, **2a**, and **3a**. Yields of **2a** and **3a** were determined using *n*-hexadecane as internal standard on glpc. **2a**[14] (77%) had ir (KBr) 2917 (m), 1491 (s), 1085 (m), and 805 cm^{-1} (s); mass spectrum (80 eV) *m/e* (rel intensity) 246 (52), 124 (31), 123 (100), 91 (47), and 45 (59). **3a**[15] (7%) had ir (neat) 3022 (w), 2917 (s), 1498 (s), 1443 (s), 1099 (s), 810 (s), 729 (w), and 709 cm^{-1} (w); mass spectrum (80 eV) *m/e* (rel intensity) 138 (100), 137 (19), 123 (36), 91 (16), and 45 (43).

4-*N*,*N*-Dimethylaminophenyl Thiolacetate (1b).—A solution of **2b** (5 g, 0.017 mol), 20 ml of acetic anhydride, and 20 ml of acetic acid was refluxed for 3 hr over 5 g of Zn and gave white crystals (recrystallized from EtOH): 4.3 g (67%); mp 81° (lit.[11] mp 80–81°); ir (KBr) 2884 (s), 1691 (s), 1597 (s), and 637 cm^{-1} (s); uv max (cyclohexane) 270 mμ (ε 26,000); mass spectrum (80 eV) *m/e* (rel intensity) 195 (32), 154 (13), 153 (100), 152 (90), and 120 (39).

Photolysis of 1b.—A deoxygenated solution of 0.237 g (0.0012 mol) of **1b** in 15 ml of cyclohexane was irradiated for 3 hr to give a mixture of **1b**, **2b**, and **3b**. The yield of **3b** was determined by glpc using benzyl tolyl sulfide as internal standard. **3b**[16] (7%) had mass spectrum (80 eV) *m/e* (rel intensity) 167 (52), 166 (29), 153 (14), 152 (100), 151 (61), and 45 (29). The mixture was triturated with ethanol and the yellow precipitate isolated was **2b**: 0.11 g (77%); mp 117° (lit.[17] mp 118°); ir (KBr) 2895 (m), 1579 (s), 1359 (s), and 808 cm^{-1} (s); mass spectrum (80 eV) *m/e* (rel intensity) 304 (8), 273 (36), 254 (10), 240 (30), 154 (13), 153 (94), 152 (100), 136 (30), and 120 (38).

4-Nitrophenyl Thiolacetate (1c).[18]—Acetic anhydride (16.5 g, 0.16 mol) was added to 25 g (0.16 mol) of 4-nitrothiophenol together with 5 drops of triethylamine. After 5 hr the yellow solid was recrystallized (50:50 NC_6H_{14}–THF) to 12 g (48%) of **1c**: mp 76–78°; ir (KBr) 3116 (m), 1716 (s), 1607 (s), 1480 (m), 1405 (m), and 747 cm^{-1} (s); uv max (cyclohexane) 285 mμ (ε 11,000) and 227 (5600); mass spectrum (80 eV) *m/e* (rel intensity) 197 (48), 156 (10), 155 (77), 139 (40), 125 (87), 43 (61), and 42 (60).

Photolysis of 1c.—A deoxygenated solution of 0.0213 g (0.108 mmol) of **1c** in 15 ml of cyclohexane was irradiated for 3 hr. The disulfide **2c** precipitated to give 0.0070 g (90%): mp 176–178° (lit.[19] mp 179–181°); ir (KBr) 1575 (m), 1490 (s), 1450 (m), 1330 (s), 850 (s), and 730 cm^{-1} (s). The solution was evaporated and analyzed on glpc, which showed the sulfide **3c** (8%) (lit.[20] mp 72°): mass spectrum (70 eV) *m/e* (rel intensity) 153 (100), 152 (93), 137 (30), 120 (64), and 109 (20).

4′-Tolyl Thiol-4-phenylbutyrate (4).—4-Phenylbutyryl chloride[21] (**29**) was prepared from thionyl chloride and 4-phenylbutanoic acid. A solution of 14.8 g (0.0815 mol) of **29** in 100 ml of dry ether was added to a solution of 10.1 g (0.0815 mol) of **7** and 6.4 g (0.0815 mol) of pyridine in 250 ml of ether maintained at 0°. The ether was washed (5% HCl, H_2O), dried ($MgSO_4$), filtered, and evaporated. The distilled residue was the ester **4**: 17.6 g (80%); bp 187° (5 mm); ir (CCl_4) 3030 (s), 2930 (s), 1705 (s), 1450 (s), and 1160 cm^{-1} (s); nmr δ 2.13 (quintet, 2, $J = 7.0$ Hz), 2.40 (s, 3), 2.60 (t, 4, $J = 7.0$ Hz), and 7.22 (s, 9); mass spectrum (70 eV) *m/e* (rel intensity) 270 (10), 147 (75), 124 (24), 123 (10), 91 (100), and 77 (10).

Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71; S, 11.86. Found: C, 75.51; H, 6.75; S, 12.06.

Photolysis of 4.—A deoxygenated solution of **4** (0.119 g, 0.436 mmol) in 15 ml of cyclohexane was irradiated for 3 hr and then evaporated to give a residue which was analyzed with glpc using triphenylmethane as internal standard. The residue contained **5** (6%), **6** (9%), **7** (7%), **8**[22] (36%), **2a** (75%), and **9** (2%). The compounds **5**, **6**, **7**, **8**, and **2a** were identified by comparison of mass spectral data with those of authentic samples. **5** had mass spectrum (70 eV) *m/e* (rel intensity) 120 (19), 118 (13), 117 (17), and 91 (100); **6**, 104 (100), 103 (41), and 78 (31); **7**, 124 (100), 91 (26), and 78 (32); **8**, 148 (5), 104 (100), and 91 (53). The sulfide **9** and **2a** were not separable on glpc but the yield of **9** was estimated from mass spectral analysis.

3-Phenylpropyl 4′-Tolyl Sulfide (9).—A solution of 10.7 g (0.054 mol) of 3-bromopropylbenzene in 80 ml of ethanol was added to a solution of 3.03 g (0.054 mol) of KOH and 6.7 g (0.054 mol) of **7** in 175 ml of EtOH at 0°. The mixture was stirred overnight and filtered and the filtrate was evaporated to give a residue which was dissolved in ether and washed (5% HCl, H_2O), dried ($MgSO_4$), filtered, and evaporated. The residue was dis-

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tilled to give an oil **9**: 10.2 g (78%); bp 150° (0.18 mm); ir (CCl_4) 3070 (s), 2900 (s), 1600 (m), 1480 (s), and 1430 cm^{-1} (s); nmr δ 1.95 (quintet, 2, J = 7.0 Hz), 2.27 (s, 3), 2.75 (t, 4, J = 7.0 Hz), 7.07 (s, 4), 7.15 (s, 5); mass spectrum (70 eV) *m/e* (rel intensity) 242 (33), 137 (10), 124 (91), 91 (100), and 77 (18).

Anal. Calcd for $C_{16}H_{18}S$: C, 79.31; H, 7.49; S, 13.20. Found: C, 79.38; H, 7.56; S, 12.81.

Phenyl 4-Toluenethiolacetate (10).—To an ethereal solution of 7.04 g (0.05 mol) of **7** and 5.8 g of Et_3N at 0° was added 8.81 g (0.057 mol) of phenylacetyl chloride to give 10.4 g (80%) of **10**: mp 60–62° (lit.[23] mp 59–61°); ir (CCl_4) 3030 (s), 2920 (m), 1700 (s), 1600 (m), 1480 (s), and 1460 cm^{-1} (s); nmr (CCl_4) δ 2.43 (s, 3), 3.85 (s, 2), 7.25 (s, 4), and 7.35 (s, 5); mass spectrum (70 eV) *m/e* (rel intensity) 242 (7), 124 (42), 118 (100), and 91 (93).

Photolysis of 10.—A deoxygenated solution of 0.142 g (0.59 mmol) of **10** in 15 ml of cyclohexane was irradiated for 3 hr and then evaporated, and the residue was analyzed in glpc with triphenylmethane was internal standard. The mixture contained **12** (28%), **13** (13%), and **2a** (35%). The compounds were identified by mass spectrometry: **12**, mass spectrum (70 eV) *m/e* (rel intensity) 182 (53), 91 (100), and 77 (17); **13**, mp 65–66° (lit.[24] mp 64–66°), mass spectrum (70 eV) *m/e* (rel intensity) 200 (19), 109 (6), and 91 (100).

4′-Tolyl Benzenethiolacetate (11).—The ester **11** was prepared by a similar procedure as reported for **10**. We obtained 3.3 g (20%) of **11**: mp 35–37° (lit.[23] mp 36–37°); ir (CCl_4) 3050 (m), 2950 (s), 1710 (s), 1475 (s), and 1415 cm^{-1} (s); nmr (CCl_4) δ 2.43 (s, 3), 3.85 (s, 2), 7.17 (s, 5), and 7.37 (s, 4); mass spectrum (70 eV) *m/e* (rel intensity) 242 (3), 133 (9), 110 (5), 109 (9), 105 (100), and 77 (13).

Photolysis of 11.—A deoxygenated solution of 0.151 g (0.62 mmol) of **11** in 15 ml of cyclohexane was irradiated for 3 hr and evaporated to give a residue which was analyzed by glpc with triphenylmethane as standard. The residue contained **14** (18%), **15**[24] (3%), **16** (25%), **17** (8%), **18** (11%), and **19**[25] (7%). The products were identified by mass spectrometry. **14** had mass spectrum (70 eV) *m/e* (rel intensity) 210 (16), 105 (100), 79 (10), and 77 (12); **15** had mass spectrum (70 eV) *m/e* (rel intensity) 214 (15), 109 (5), 105 (100), and 77 (12); **16** had mass spectrum (70 eV) *m/e* (rel intensity) 218 (77), 109 (100), and 77 (25); **17** had mass spectrum (70 eV) *m/e* (rel intensity) 106 (48), 105 (25), 91 (100) and 77 (14); **18** had mass spectrum (70 eV) *m/e* (rel intensity) 110 (100), 109 (31), 84 (23), and 77 (21); **19** had mass spectrum (70 eV) *m/e* (rel intensity) 208 (100), 178 (61), and 91 (17).

Photolysis of 10 and 11.—A solution of 0.076 g (0.31 mmol) of **10** and **11** in 15 ml of cyclohexane was irradiated for 3 hr and evaporated to give a residue which was analyzed on glpc. The mixture contained **12** (6%), **14** (3%), **22** (2%), **13** (5%), **15** (2%), **20**[26] (6%), **21**[24] (11%), **16** (16%), **3a** (40%), and **23**[27] (5%). The products were identified by mass spectrometry. **20** had mass spectrum (70 eV) *m/e* (rel intensity) 200 (19), 109 (6), 91 (100), and 77 (4); **21** had mass spectrum (70 eV) *m/e* (rel intensity) 228 (65), 123 (17), 105 (100), 91 (21), 79 (51), and 77 (56).

Photolysis of 18 and 1a.—A deoxygenated solution of 0.14 g (1.3 mmol) of **18** and 0.22 g (1.3 mmol) of **1a** in 15 ml of cyclohexane was irradiated for 3 hr, evaporated, and analyzed using glpc with *p*-xylene as standard. The mixture contained **7** (5%), **18** (4%), **3a** (1%), **25** (5%), **1a** (9%), **24** (3%), **16** (32%), **2a** (14%), **23** (16%), **26** (2%), and **27** (1%). The products were identified by mass spectrometry. **26**[28] had mass spectrum (70 eV) *m/e* (rel intensity) 192 (23), 110 (100), 109 (16), and 83 (14); and **27**[28] had mass spectrum (70 eV) *m/e* (rel intensity) 206 (20), 124 (100), and 91 (56).

Photolysis of 7 and 24.—A solution of 0.19 g (1.5 mmol) of **7** and 0.22 g (1.5 mmol) of **24** was photolyzed and analyzed in the same way as **18** and **1a**. The mixture contained **7** (6%), **18** (8%), **1a** (11%), **24** (28%), **16** (4%), **2a** (22%), **23** (9%), **26** (1%), and **27** (2%).

Phenyl Thiolacetate (24).—The ester **24** was prepared by a method similar to that for **1c**. We obtained 8.6 g (57%): bp 110–111° (11 mm) [lit.[18] bp 91° (7 mm)]; mass spectrum (80 eV) *m/e* (rel intensity) 152 (33), 110 (91), 109 (53), 77 (16), and 43 (100). Other spectral data are the same as reported by others.[3,13]

Registry No.—**1a**, 10436-83-6; **1b**, 14297-63-3; **1c**, 15119-62-7; **2a**, 103-19-5; **2b**, 5397-29-5; **3a**, 623-13-2; **3b**, 2388-51-4; **4**, 38644-96-1; **7**, 106-45-6; **9**, 38644-97-2; **10**, 38644-98-3; **11**, 18241-65-1; **18**, 108-98-5; **14**, 934-87-2; 4-phenylbutyryl chloride, 18496-54-3; 3-bromopropylbenzene, 637-59-2.

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Synthesis of Octahydrothiopyrano[3,2-*b*]thiopyran and Certain Derivatives[1]

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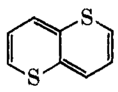
Octahydrothiopyrano[3,2-*b*]thiopyran (**10a**) has been prepared by a multistep synthesis in which the enamine, 3-pyrrolidinothiacyclohex-2-ene (**6**), served as a key intermediate. The title compound (**10a**), isolated from a liquid mixture of isomeric materials, was obtained as a pure crystalline isomer (mp 68.5–70°) and assigned the trans configuration on the basis of nmr spectral parameters. Sodium metaperiodate oxidation of **10a** yielded a well-defined monosulfoxide (**11**) which underwent a Pummerer dehydration in acetic anhydride to afford a mixture of two isomeric hexahydrothiopyrano[3,2-*b*]thiopyrans (**12a** and **12b**).

The synergistic interaction of theoretical[3] and synthetic investigations during the past several years has led to an unusual variety of new heterocyclic sulfur compounds, of which cyclopenta[*c*]thiopyran,[4] 1-phenyl-1-thianaphthalene,[5] and thienothiapyrylium cations[6,7] have been of particular interest as nonclassical 10-π-electron systems. Among other novel thia heterocycles, whose syntheses have not yet been realized, thiopyrano[3,2-*b*]thiopyran (**1**) appeared to be an especially attractive goal for synthesis, since this



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