gen-bonded complexes of the type II at low concentrations. We have also shown the influence of various solvents on intramolecular hydrogen bonding.

Registry No.—Ia, 26823-99-4; Ib, 26824-00-0.

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The Ultraviolet Irradiation of *S*-Phenyl Thiolacetate[1-3]

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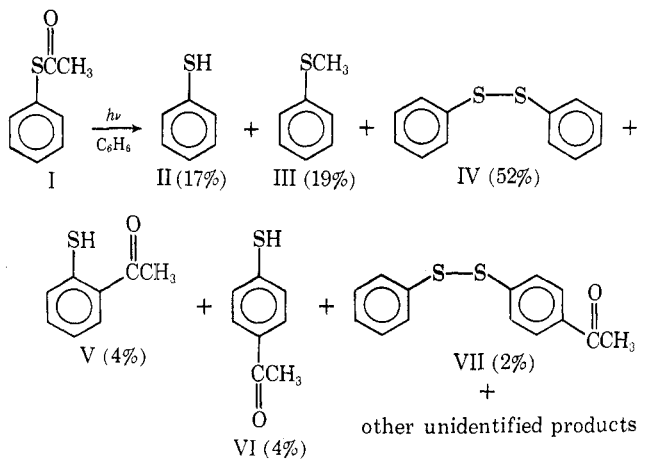
A recent communication[4] prompted us to report the results of our study of the ultraviolet irradiation of S-phenyl thiolacetate (I). When a 0.1 *M* solution of I in benzene was irradiated for 4 hr with a medium-pressure mercury lamp, the products shown in Scheme I were

SCHEME I



produced. Approximately 40% of the starting material was recovered. The products were isolated by preparative gas chromatography and identified by ir and nmr spectroscopy.

Products II, III, and IV were identified by comparison with authentic samples. The structure assignments for the photo-Fries reaction products (V and VI) were made from their ir and nmr spectra, which we believe are definitive. The nmr peak, attributable to the S–H proton, was shifted from δ 3.40 for VI to δ 5.10 for V. This type of shift is always observed when protons, which are capable of hydrogen bonding, are ortho to carbonyl groups.[5] The nmr of VI also exhibited a symmetrical AB pattern (really AA′XX′) centered at δ 7.45. This is typical of benzene compounds which have different substituents in the para positions.[6] The structure assignment for compound VII is consistent with the spectral data. The ir of VII exhibited strong bands at 688 and 742 cm^{-1} which are indicative of the monosubstituted benzene moiety, as well as a strong band at 890 cm^{-1} which can be attributed to para-disubstituted benzene.[7] One of the small peaks which could not be isolated could be the ortho analog of VII.

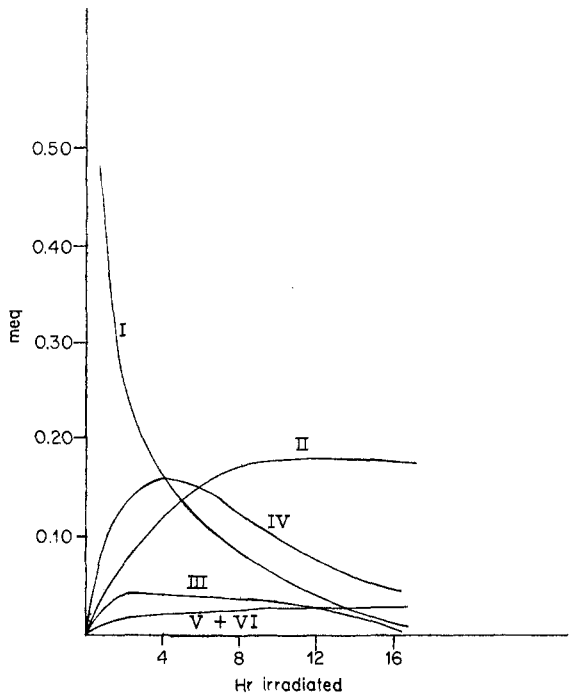


Figure 1.—0.1 *M* solution of *S*-phenyl thiolacetate in benzene.

The ratio of these products changed significantly as irradiation time was increased. As shown in Figure 1, the amount of II increased steadily while III and IV increased to a maximum at about 4 hr, then decreased in yield until the light was turned off after 16 hr. These results show that this is not a simple reaction. We feel the change in product ratios is due to secondary reactions. For example, diphenyl disulfide has been reported to form thiophenol when irradiated by ultraviolet light.[8] Compounds similar to thioanisole have been reported to form disulfides when irradiated.[9] The disulfide then would react to form thiols. We obtained thiophenol when we irradiated either thioanisole or diphenyl disulfide under our reaction conditions.

Table I gives a summary of the results of the irradiation of I in various solvents. The samples were irradiated until polymer build-up prevented further reaction. No products were observed when I was irradiated in either methyl carbitol ($CH_3OCH_2CH_2OH$) or ethanol. When a solution of I in benzene was irradiated by a low-pressure mercury lamp, the products were the same but ratios were different (see Table I). Apparently thioanisole is converted to diphenyl disulfide faster than the

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(1) Supported by the Brigham Young University Research Division and the United Fund of Utah County.

(2) Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer purchased under the National Science Foundation Grant GP-6837.

(3) Presented at the Pacific Northwest Regional Meeting of the American Chemical Society, Salt Lake City, Utah, June 1969.

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(5) See R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 122.

(6) See ref 5, p 127.

(7) See Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 26.

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(9) W. Carruthers, *Nature*, **208**, 908 (1961).

TABLE I
IRRADIATION OF S-PHENYL THIOLACETATE USING A MEDIUM-PRESSURE LAMP

Solvent	Time, hr	% conversion	II	III	IV	V	VI	VII
Benzene	4	60	17	19	52	4	4	2
Benzene[a]	6	67	13	3	71	1	2	4
THF	48[b]	40	19	5	77	3	2	
Ether	48[b]	30	4	8	87	3	2	3
Cyclohexane	3	35	11	13	61	2	1	3

[a] A low-pressure Hanovia lamp was used. [b] Sample was in a quartz tube.

diphenyl disulfide is converted to thiophenol by the 2537-Å light.

We believe that the starting material cleaves under the influence of ultraviolet light to form C_6H_5S and $COCH_3$ radicals. The phenyl sulfide radical can then abstract a hydrogen atom to form thiophenol (II) or dimerize to form the disulfide IV. Occasionally, before the radicals separate, CO is liberated and the resulting phenylthiyl and methyl radicals combine to form thioanisole (III). Even less occasionally, the $COCH_3$ and phenyl sulfide radicals react to form the photo-Fries products V and VI. Intramolecular formation of products III, V, and VI has not been demonstrated; however, we believe that the reaction is intramolecular as are the corresponding esters.[10] Since irradiation of thiophenol did not yield diphenyl disulfide, we feel that VII was not formed by the irradiation of VI but rather by the combination of a phenylthiyl radical and *p*-acetylphenylthiyl radical. Thiophenol (II) is also formed by the secondary photolysis of III and IV as discussed above.

The source of the abstracted hydrogen (in thiophenol formation) is not known. Schaafsma and coworkers[11] have proposed that the hydrogen atom was abstracted from another phenylthiyl radical. Polymer would be a by-product of this reaction.[11] Polymer was observed in all our reactions. We observed no solvent dimer in any reaction which indicates that the solvent was not the source of the hydrogen atom.

Experimental Section

Materials and Apparatus.—Thiophenol and thioanisole were purchased from Aldrich Chemical Co. Diphenyl disulfide was purchased from Eastman Chemical Co. Benzene (Baker) was purified according to the procedure of Hammond.[12] Acetic anhydride (Matheson Coleman and Bell), cyclohexane and tetrahydrofuran (MCB), dimethylformamide (Baker), and anhydrous ethyl ether and methyl carbitol (Mallinckrodt) were reagent grade and used as received.

A Hanovia 450-W medium-pressure mercury lamp and a SC 2537 low-pressure mercury lamp were used. A quartz immersion reactor was used in all immersion reactions. All ir spectra were obtained on a Perkin-Elmer 457 spectrophotometer. The nmr spectra were obtained on a Varian A-60A spectrometer.[2] A Varian 202-B vapor phase chromatograph (vpc) was used to isolate all products. *S*-Phenyl thiolacetate was prepared by the procedure of Baker and Harris[13] and was purified by vacuum distillation: bp 55–60° (1 mm); ir 1710 cm^{-1}; nmr δ 2.20 (s, 3), 7.6 (s, 5).

Irradiation Procedure.—A 0.1 *M* solution of I in the appropriate solvent was placed in the immersion reactor. A small stream of pure nitrogen was sparged into the solution for 20–40 min before irradiation began and continued during the irradiation. The usual irradiation times were 2–4 hr. For irradiation times longer than 4 hr, polymeric material had to be removed from the well or the intensity of the light was greatly reduced. The solvent was then removed under the reduced pressure of a water aspirator at 50–60°. The remaining dark, foul-smelling liquid (5 ml) was placed in a vial under N_2 to prevent oxidation of the thiol (II) to disulfide (IV). The mixture was analyzed by vpc using a 3% SE-30 on Varaport 30 column and programming the temperature from 75 to 275°. Isolation was accomplished using 10% SE-30 on acid washed Chromosorb G. Chlorobenzene was used as an internal standard in determining product yields.

The runs in methyl carbitol, dimethylformamide, tetrahydrofuran, and ether were made in quartz tubes, degassed by three freeze–thaw cycles ($\sim 10^{-4}$ Torr). The tubes were irradiated for 24 hr on a "merry-go-round"[14] through a 1-cm^2 aperture and then 24 hr fully exposed to the low-pressure lamp. They were opened and analyzed by the same procedure as described above.

Analysis of the Products.—The products were isolated on the vpc and analyzed as follows. Fraction 1 (II), 2 (III), 3 (I), and 6 (IV) had ir and nmr spectra which were the same as authentic samples.

Fraction 4 (V) exhibited the following spectra: ir 3055, 2540 (SH), 1665 (C=O), 750 cm^{-1}; nmr (CCl_4) δ 2.55 (s, 3), 5.10 (s, 1), 7.45 (m, 4).

Fraction 5 (VI) exhibited the following spectra: ir 3050, 2550 (SH), 1680 (C=O), 820 cm^{-1}; nmr (CCl_4) δ 2.47 (s, 3), 3.40 (s, 1), 720 (d, 2), 7.70 (d, 2).

Fraction 7 (VII) exhibited the following spectra: ir 3055, 1675 (C=O), 890, 742, 688 cm^{-1}; nmr (CCl_4) δ 2.42 (s, 3), 7.4 (m, 9).

Registry No.—I, 934-87-2; V, 26824-02-2; VI, 3814-20-8; VII, 26824-04-4.

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A Reassignment of Structure to the Scholtz "Pyrrolo[1,2-*a*]indole"

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A literature search for examples of the pyrrolo[1,2-*a*]-indole ring system, an important subunit of the mitomycin antibiotics,[2] revealed an early report of its preparation.[3] The *N*-acetylation and subsequent cyclodehydration of *N*-phenacylanthranilic acid (**1**) reportedly furnished the pyrrolo[1,2-*a*]indole **2a** (or some tautomer of it). This tricylic material was then hydrolyzed to the supposed indolylacrylic acid (**3a**). Our reinvestigation of these compounds, in the light of current spectroscopic structural analysis, has resulted in a reassignment of structure to these products. The phenacylanthranilic acid **1**, mp 183–184°, corresponding to the literature assignment, was prepared by alkylation of isatoic anhydride followed by hydrolysis rather than by

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