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.

(10) M. R. Sandner, E. Hedaya, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 7249 (1968).

(11) Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, *Tetrahedron*, **60**, 76, (1960).

(12) G. S. Hammond, S. C. Shim, and S. P. Van, *Mol. Photochem.*, **1**, 103 (1969).

(13) A. W. Baker and G. H. Harris, *J. Amer. Chem. Soc.*, **82**, 1923 (1960).

(14) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

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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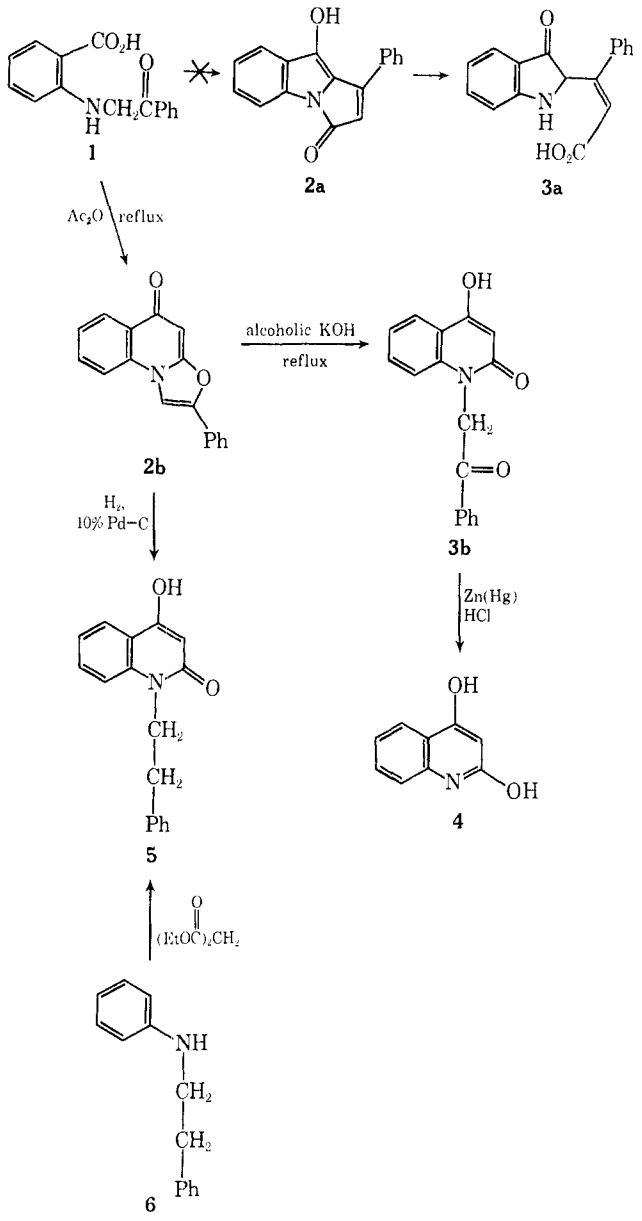
(1) This work was supported in part by Public Health Service Grants GM 12758 and CA 11421.

(2) G. O. Morton, G. E. Van Lear, and W. Fulmor, *J. Amer. Chem. Soc.*, **92**, 2588 (1970); the latest paper on the structural assignment of a member of the mitomycin class.

(3) (a) M. Scholtz, *Chem. Ber.*, **51**, 1645 (1918); (b) R. Wegscheider, *ibid.*, **52**, 1705 (1919).

the direct alkylation of anthranilic acid as in the original work. The cyclodehydration product, mp 276–278°, does not appear to have a carbonyl in a five-membered ring. It does not exhibit the characteristics of an enol. Its nmr spectrum reveals two uncoupled protons in deshielded environments which are not part of the aromatic envelope. In general, its uv and ir data are quite consistent with data for 2-alkoxy-4-quinolones.[4] We formulate the cyclodehydration product, mp 288°, as the oxazolo[3,2-*a*]quinoline **2b** (Scheme I). Thus, the

SCHEME I



hydrolysis product, mp 322–324° dec, of tricyclic **2b** is best formulated as the 4-hydroxy-1-phenacylcarbostyril **3b**, the spectral data of which are again in accord with the literature examples.[4] Further, zinc amalgam cleavage[5] of **3b** affords the parent quinoline **4**, identified by its superimposable ir and undepressed mixture melting point with an authentic sample.[6] This experiment demonstrates that **3b** has a quinoline framework. However, **3b** is obtained by base treatment of **2b** and one could argue that these conditions can effect retro-aldol and retro-Michael reactions followed by recyclizations, with the result being that the quinoline framework of **3b** is not at all related to **2b**. Thus, **2b** was subjected to catalytic hydrogenolysis, the product of which proved to be 4-hydroxy-1-phenethylcarbostyril (**5**), which was identical with a sample which was independently synthesized from phenethylaniline **6** and diethyl malonate.[7] To the best of our knowledge, **2b** is the first example of a neutral oxazolo[3,2-*a*]quinoline, although the ring system as the oxazolo[3,2-*a*]quinolinium perchlorate has been prepared.[8]

(4) H. Rapoport and K. G. Holden, *J. Amer. Chem. Soc.*, **82**, 4395 (1960).
(5) J. B. Hendrickson and C. Kandall, *Tetrahedron Lett.*, 343 (1970).
(6) Available commercially as the sodium salt from K and K Laboratories, Plainview, N. Y.

Experimental Section

***N*-Phenacylanthranilic Acid (1).**—To a mixture of 27.7 g (0.17 mol) of isatoic anhydride dissolved in 200 ml of dimethylformamide and 18 g (0.22 mol) of sodium carbonate was added 26.2 g (0.17 mol) of phenacyl chloride dissolved in 200 ml of dimethylformamide. The reaction mixture was allowed to stir vigorously over a 24-hr period at room temperature. After the excess sodium carbonate was filtered off, the reaction mixture was poured into 230 ml of 10% sodium hydroxide and acidified to pH 5 with 0.5 *N* aqueous hydrochloric acid. The crude product precipitated from the acidified solution and was subsequently filtered. After recrystallization from 95% ethanol, a total of 14.1 g (33%) of *N*-phenacylanthranilic acid was collected: mp 183–184° (lit.[3a] mp 190°); uv max (95% C_2H_5OH) 224 mμ (log ε 4.56), 254 (4.37), 282 (3.58), and 330 (3.79); ir (KBr) 1684, 1694, 2934, and 3339 cm^{-1}; nmr (acetone-d_6) δ 4.91 (s, 2 H), and 6.51–8.88 ppm (br envelope, 11 H).

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.45; H, 5.14; N, 5.38.

2-Phenyl-5-oxooxazolo[3,2-*a*]quinoline (2b).—*N*-Phenylacylanthranilic acid (1) [12.10 g (0.047 mol)] was refluxed with 121 ml of acetic anhydride for 3 hr. The reaction mixture was then poured into 150 ml of water and yielded a flaky substance after hydrolysis of the anhydride. The crude material was recrystallized from boiling pyridine, yielding 6.64 g (54%) of 2-phenyl-5-oxooxazolo[3,2-*a*]quinoline: sublimes 180–190° (0.2 mm); mp 276.5–278° (lit.[3a] mp 288°); uv max (95% C_2H_5OH) 218 mμ (log ε 3.96), 221 (4.01), 259 (3.52), 290 (3.66), and 340 (3.92); ir (KBr) 1200, 1550, 1580, 1620, 1655, and 3070 cm^{-1}; nmr (glacial acetic acid) δ 6.73 (s, 1 H), 7.13–8.46 (br envelope, 9 H), and 8.65 ppm (s, 1 H).

Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 77.99; H, 4.25; N, 5.48.

4-Hydroxy-1-phenacylcarbostyril (3b).—A mixture of 6.01 g (0.023 mol) of 2-phenyl-5-oxooxazolo[3,2-*a*]quinoline (**2b**), 90 ml of 95% ethanol, and 15 g of potassium hydroxide dissolved in 30 ml of water was refluxed. After complete solution of the solid (*ca.* 40 min), the liquid was evaporated on a rotary vacuum evaporator leaving a solid mass which was dissolved in hot water and recovered by acidification of the solution to pH 5 with 0.5 *N* aqueous hydrochloric acid. Recrystallization from glacial acetic acid yielded 5.75 g (90%) of 4-hydroxy-1-phenacylcarbostyril: sublimes 265–285° (760 mm); 322–324° dec (lit.[3a] 300° dec); uv (95% C_2H_5OH) 205 mμ (log ε 3.31), 231 (3.60), 274 (2.92), 284 (2.92), and 319 (2.67); ir (KBr) 1545, 1565, 1595, 1640, 2920, and 3424 cm^{-1}; nmr (trifluoroacetic acid) δ 6.06 (s, 2 H), 7.00 (s, 1 H), and 7.21–8.60 ppm (br envelope, 10 H).

Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.01. Found: C, 72.99; H, 4.76; N, 5.08.

Hydrogenation of 2-Phenyl-5-oxooxazolo[3,2-*a*]quinoline (2b).—A sample of 0.301 g (1.15 mmol) of 2-phenyl-5-oxooxazolo-[3,2-*a*]quinoline (**2b**) was dissolved in 5 ml of glacial acetic acid and added *via* a dropping funnel to the prereduced catalyst, 0.046 g of 10% Pd–C in acetic acid. As the reaction proceeded, the hydrogenated material precipitated out of the solvent. Hydrogen (2 equiv) was absorbed over a period of 10 hr. At the end of this time, the reaction mixture was removed from the hydrogena-

(7) E. Ziegler and R. Wolf, *Monatsch. Chem.*, **96**, 418 (1965).
(8) (a) C. K. Bradsher and M. F. Zinn, *J. Heterocycl. Chem.*, **4**, 66 (1967); (b) A. Lawson and D. H. Miles, *J. Chem. Soc.*, 2865 (1959).

tor and was heated until the precipitated material redissolved. After the mixture was allowed to stand overnight at room temperature, pure 4-hydroxy-1-phenethylcarbostyril **5** (85%) was collected. This material, mp 255–256°, was identical (uv, ir, and nmr) with that prepared *via* *N*-phenethylaniline (**6**).

4-Hydroxy-1-phenethylcarbostyril (**5**) *via* ***N*-Phenethylanilin** (**6**).—A solution of 3.00 g (0.015 mol) of *N*-phenethylaniline (**6**) and 1.034 g (0.0076 mol) of diethyl malonate was placed under an atmosphere of nitrogen. The system was heated slowly in a Wood's metal bath to a temperature of 250–260°. The reaction mixture liberated 0.4 ml of ethanol within 15 min which was collected in a Dean–Stark apparatus; this quantity, however, was only one-half the expected amount. Therefore, the system was heated for an additional 20 min at the same temperature but failed to produce any additional ethanol. The reaction mixture was allowed to cool to room temperature, and *ca.* 10 ml of acetone was then added which caused a precipitate to form which was filtered, yielding 0.0801 g (4%) of product which was identified as 4-hydroxy-1-phenethylcarbostyril: mp 255–256°; uv (95% C_2H_5OH) 213 mμ (log ε 4.05), 226 (4.34), 232 (4.35), 275 (3.58), and 285 (3.45); ir (KBr) 1635, 2910, and 3390 cm^{-1}; nmr (trifluoroacetic acid) δ 3.20 (t, 2, J = 7 Hz), 4.86 (t, 2, J = 7 Hz), 6.92 (s, 1 H), and 7.00–8.60 ppm (br envelope, 10 H).

Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.82; H, 5.68; N, 5.34.

Further heating of the mother liquors at 140° for 4 hr with polyphosphoric acid brought the overall yield of **5** obtained from the reaction to 25%.

***N*-Phenethylaniline** (**6**).[9]—A mixture of 26.12 g (0.28 mol) of freshly distilled aniline, 6.61 g (0.078 mol) of sodium bicarbonate, and 10 ml of water was refluxed under an atmosphere of nitrogen. Freshly distilled phenethyl bromide [12.88 g (0.069 mol)] was added by means of an addition funnel during the first 2 hr of reflux; the mixture was allowed to reflux an additional 2.25 hr. The reaction mixture was then allowed to come to room temperature and filtered, and the aqueous and organic layers separated. The latter was washed with a saturated solution of sodium chloride. The amines were dried over sodium sulfate and again filtered. Separation of the amines was accomplished by vacuum distillation using a fractionating column; one fraction distilled at 26–28° (0.025 mm) and was identified as aniline.

The other fraction contained 8.45 g (54%) of *N*-phenethylaniline which distilled at 120–125° (0.025 mm): uv (95% C_2H_5OH) 212 mμ (log ε 4.32), 250 (4.39), and 295 (3.52); ir (CCl_4) 1600, 2925, 3020, and 3400 cm^{-1}; nmr (CCl_4) δ 2.75 and 3.25 (A_2B_2, J = 7 Hz, 4 H), 3.39 (s, 1 H), and 6.28–7.34 ppm (br envelope, 10 H). An exchangeable proton was seen at δ 3.39 with the appearance of a water peak at δ 4.67.

Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.30; H, 7.62; N, 7.18.

2,4-Dihydroxyquinoline (**4**) *via* ***N*-Phenacyl-2,4-dihydroxyquinoline** (**3b**).—A mixture of 0.25 g of mossy zinc, 0.025 g of mercuric chloride, 0.01 ml of concentrated hydrochloric acid, and 0.4 ml of water was refluxed for 5 min in a 10-ml round-bottom flask, followed by the addition of 0.2 ml of water, 0.25 ml of toluene, 0.01 ml of glacial acetic acid, and 0.200 g (0.0007 mol) of *N*-phenacyl-2,4-dihydroxyquinoline (**3b**), respectively. The mixture was refluxed continuously for 24 hr with the addition of 0.4 ml of concentrated hydrochloric acid every 6 hr. After the mixture was cooled to room temperature, 0.082 g (73%) of pure product precipitated and was identified by its melting point and superimposable ir as 2,4-dihydroxyquinoline.

2,4-Dihydroxyquinoline (**4**) *via* **Hydrolysis of Its Sodium Salt.**—A sample of 6.471 g of the sodium salt of 2,4-dihydroxyquinoline was dissolved in about 40 ml of hot water. Material that remained after the solution came to room temperature was filtered off. The aqueous filtrate was acidified to pH 5–6 by dropwise addition of 5% aqueous hydrochloric acid. In this manner, 4.215 g (76%) of 2,4-dihydroxyquinoline was collected: mp 354–355° (lit.[10] mp 355°); ir (KBr) 1230, 1325, 1670, 2850, and 3350 cm^{-1}.

Registry No. —**1**, 732-64-9; **2b**, 26630-29-5; **3b**, 26630-30-8; **5**, 26630-31-9; **6**, 1739-00-0.

(9) H. Gilman, Ed., "Organic Syntheses," Coll. Vol. 1, Wiley, New York, N. Y., 1932, p 97.

(10) E. H. Rodd, Ed., "Chemistry of Carbon Compounds," Vol. 4A, Elsevier, New York, N. Y., 1957, p 624.

A Study of the Mechanism of the Photoisomerization of 2-Phenylisatogen to 2-Phenyl-4*H*-3,1-benzoxazin-4-one[1]

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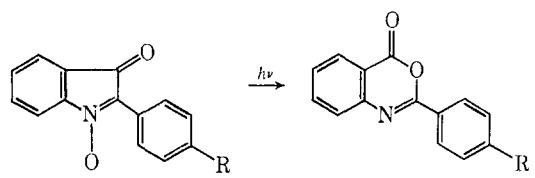
Recently we have described the photoisomerization of 2-phenylisatogen (**1a**) to 2-phenyl-4*H*-3,1-benzoxazin-4-one (**2a**) (eq 1), in various solvents with various



(1)

1a, R = H; **b**, R = Br **2**

light sources.[3] With 5.6×10^{-3} M concentration of 2-phenylisatogen in cyclohexane, there is almost quantitative conversion to **2a** after 3 hr of irradiation with a 450-W medium-pressure total immersion lamp.

The reaction, followed by ultraviolet spectra at several stages, shows isosbestic points at 255 and 300 mμ in solvents cyclohexane, cyclohexene, chloroform, absolute ethanol, 95% ethanol, and glacial acetic acid. The presence of isosbestic points indicates that there is no photostationary intermediate (*i.e.*, there is no intermediate with a lifetime of more than several seconds).

Unusual behavior at 2537-Å irradiation was displayed in solvents benzene, toluene, acetone, and methylisobutyl ketone. In each solvent, irradiation at 2537 Å gives rise to a photostationary intermediate, with absorption maxima in benzene solution at 356, 378, and 400 mμ (vibronic spacing = 1450–1475 cm^{-1}). Upon continued irradiation the intermediate is consumed and 2-phenyl-4*H*-3,1-benzoxazin-4-one, **2a**, is almost quantitatively formed. With 3500-Å-irradiation the intermediate is not formed in these solvents and the superimposed uv spectra of the reaction at various times show an isosbestic point (at 300 mμ) identical with the first six solvents.

It appears that the reaction proceeds by way of a singlet mechanism and that the aromatic and ketonic solvents behave as triplet sensitizers, thus allowing another reaction to take place.

Quantum yields were found to be independent of time and intensity of irradiation, and the presence of oxygen, but dependent on wavelength, concentration, solvent, and temperature.

The quantum yields of formation of **2a** in cyclohexane solution are shown in Table I. The decreased quantum yield in the presence of 10^{-2} M *m*-methoxyacetophenone can be accounted for by the fact that *m*-methoxyaceto-

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(3) D. R. Eckroth and R. H. Squire, *Chem. Commun.*, 312 (1969); D. R. Eckroth, *ibid.*, 465 (1970).