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.

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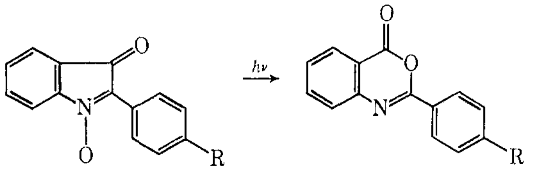
Recently we have described the photoisomerization of 2-phenylisatogen (**1a**) to 2-phenyl-4*H*-3,1-benzoxazin-4-one (**2a**) (eq 1), in various solvents with various



(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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[1] Part of this work was presented as a paper at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, ORGN 13.

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

TABLE I

Φ_{dis} OF **1a**[a]

Solvent	Temp, °C	λ, mμ (±15 mμ)	Φ_{dis} × 10^3	Molar concn of **1a**
Cyclohexane	25	254	15.1	1×10^{-3}
Cyclohexane	25	265	12.5	1×10^{-3}
Cyclohexane	25	295	8.0	1×10^{-3}
Cyclohexane	25	302	5.6	1×10^{-3}
Cyclohexane	25	305	6.2	1×10^{-3}
Cyclohexane	25	350	0.0	4×10^{-3}
Cyclohexane	45	305	7.2	1×10^{-3}
Cyclohexane	60	254	16.0	1×10^{-3}
Cyclohexane	60	265	14.3	1×10^{-3}
Cyclohexane	60	295	9.2	1×10^{-3}
Cyclohexane	60	305	7.4	1×10^{-3}
Cyclohexane with 10^{-2} *M* *m*-methoxyacetophenone	25	302	3.2	1×10^{-3}
Ethyl bromide–cyclohexane (1:2 vol ratio)	25	305	4.6	1×10^{-3}
Absolute ethanol	25	254	6.0	1×10^{-3}

Φ_{dis} of **1b**[a]

Solvent	Temp, C°	λ, mμ (±15 mμ)	Φ_{dis} × 10^3	Molar concn of **1b**
Cyclohexane	25	254	9.1	1×10^{-3}
Cyclohexane	25	305	4.5	1×10^{-3}
Cyclohexane	60	305	5.5	1×10^{-3}

[a] Φ_{dis} measured by disappearance of absorption maximum of **1a** at 442 mμ and that of **1b** at 450 mμ. Maximum error of Φ_{dis} is ±10%.

phenone is absorbing approximately half of the light at 3025 Å.

In the presence of ethyl bromide, intermolecular spin orbit coupling[4] presumably allows rapid intersystem crossing which slows the apparently singlet reaction. Intramolecular spin orbit coupling[5] is demonstrated by the reduced quantum yields of product from 2-(*p*-bromophenyl)isatogen (**1b**).[6]

The quantum yields from benzene solutions, shown in Table II, indicate strong concentration dependence.[7]

TABLE II

Φ_{dis} OF **1a**[a]

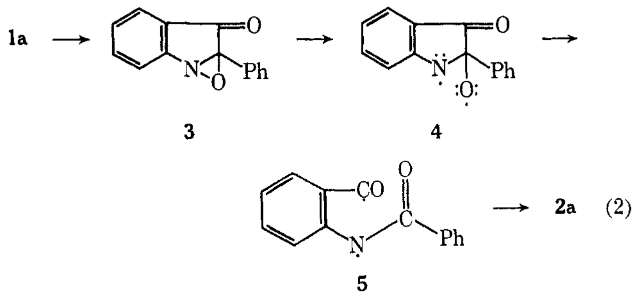
Solvent	Temp, °C	λ, mμ (±15 mμ)	Φ_{dis} × 10^4	Molar concn of **1a**
Benzene	25	254	15.7	1×10^{-3}
Benzene	25	295	24.7	1×10^{-3}
Benzene	25	302	20.6	1×10^{-3}
Benzene	25	305	23.5	1×10^{-3}
Benzene	25	305	6.2	5×10^{-3}
Benzene	25	305	4.3	1×10^{-2}
Benzene	25	305	0.4	5×10^{-2}
Benzene with 10^{-2} *M* thioxanthone	25	302	12.9	1×10^{-3}
Benzene with 10^{-2} *M* *m*-methoxyacetophenone	25	302	9.8	1×10^{-3}

[a] Φ_{dis} measured by disappearance of absorption maximum of **1a** at 442 mμ. Maximum error of Φ_{dis} is ±10%.

Triplet sensitizers such as thioxanthone and *m*-methoxyacetophenone reduce the quantum yield considerably at 3025 Å, but this is in part due to the fact that at their concentrations, they absorb roughly half of the light.

The fact that the quantum yield depends upon the concentration[8] of isatogen suggests that the reaction is sufficiently slow and that the deactivation of excited isatogen molecules with ground-state molecules occurs; *i.e.*, the compound apparently undergoes self-quenching.[7]

A possible reaction scheme could have initial conversion of the isatogen to the oxaziridine, **3**,[9] followed by N–O bond cleavage which could lead to a diradical **4**, with unpaired electrons on nitrogen and oxygen.[10] A homolytic cleavage of the C_2–C_3 bond could lead to diradical **5**. Bond formations at C_3–O and C_2–N could then lead to the benzoxazinone **2a** (eq 2). There is difficulty in rationalizing this scheme in that intermediate **5** is a form of the imine–ketene **6**, which should be trapped by a polar solvent such as ethanol in the same way as that described by Ege[11] (eq 3).



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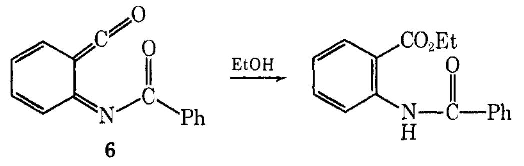
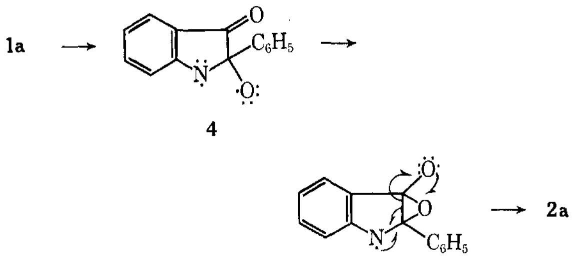


(3)

It appears that the diradical **4** must form a C_3–O bond either before or in concert with C_3–C_2 bond cleavage, in order to prevent imine–ketene formation *via* **5**[12] (eq 4).



(4)

Experimental Section

Materials.—2-Phenylisatogen (1a) was prepared according to a procedure outlined by Jones,[13] and recrystallized twice from ethanol, mp 188–190° (lit.[13] mp 189.5–190°).

2-(4′-Bromophenyl)isatogen (1b) was prepared by a modification of Jones'[13] procedure with α,*p*-dibromotoluene and recrystallized twice from ethanol, mp 183° (lit.[14] mp 183–184°).

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[4] M. Kasha and S. P. McGlynn, *Annu. Rev. Phys. Chem.*, **7**, 403 (1956).

[5] S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., p 183.

[6] There is almost quantitative conversion of **1b** to **2b**.

[7] O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969).

[8] Beer's law is obeyed at every concentration.

[9] For an excellent review, see G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).

[10] Competitive thermal processes **3** → **4** and **3** → **1a** might account for the temperature dependence.

[11] G. Ege, *Angew. Chem.*, **77**, 723 (1965). R. K. Smalley, H. Suschitsky, and E. M. Tanner, *Tetrahedron Lett.*, 2465 (1966), showed that imine–ketenes structurally similar to **6** can easily dimerize.

[12] A similar suggestion was made in the case of photochemistry of silyl ketones by A. G. Brook and J. M. Duff, *J. Amer. Chem. Soc.*, **89**, 454 (1967).

[13] D. A. Jones, Ph.D. Dissertation, University of Minnesota, 1961.

[14] F. Kröhnke and I. Vogt, *Ber.*, **85**, 376 (1952).

2-Phenyl-4*H*-3,1-benzoxazin-4-one (**2a**) was synthesized independently according to the procedure described by Bogert, *et al.*,[15] mp 124° (lit.[15] mp 124.5°).

2-(4′-Bromophenyl)-4*H*-3,1-benzoxazin-4-one (**2b**) was synthesized by a modification of Bogert's[15] procedure with *p*-bromobenzoyl chloride, mp 185–189° (lit.[16] mp 183–184°).

The cyclohexane, chloroform, benzene, and acetone were spectroscopic grade. They were further dried over magnesium sulfate and distilled through a 30-cm column. Only the middle cuts were used. The cyclohexene, toluene, and methylisopropyl ketone were reagent grade and were purified as described above. The 95% ethanol was made from absolute ethanol and distilled water. The acetic acid was reagent grade.

Typical Irradiation Experiments. With Rayonet 2537-and 3500-Å Lamps.—**1a** or **1b** (0.5 g) was dissolved in 650 ml of solvent, placed in a quartz reaction vessel fitted with a magnetic stirrer, and irradiated for an extended period of time.

With Hanovia 450-W Medium-Pressure Immersion Lamp (No Filter).—One gram of **1a** or **1b** was dissolved in 750 ml of solvent, placed in a water-cooled reaction chamber, and irradiated for 1–3 hr. The benzoxazinone (**2a** or **2b**) was separated from the unreacted starting material by sublimation (95°, 0.1 mm, 30 hr).

Quantum Yields.—For quantum-yield determinations light from a Bausch and Lomb high-intensity monochromator equipped with an Osram HBO-200W super-pressure mercury source was employed. The monochromator settings were at 254, 265, 295, 302, 305, and 350 mμ and the exit slits were set at 4 mm. Under these conditions the maximum band width was 29.6 mμ. The light passed directly into a standard glass-stoppered 10 × 10 mm silica cuvette which served as the reaction vessel. The cell was held 5.5 cm from the exit port of the monochromator in a metal compartment maintained at constant temperature by flowing water. Light incident on the reaction solution was determined by irradiating samples of actinometer solution both before and after irradiation of the reaction solution. The extent of reaction was determined by the decrease in absorbance at 442 mμ with **1a** and 450 mμ with **2a**, and the period of irradiation was such that the reaction proceeded less than 10% to completion. Calculations of quantum yields were performed with the procedure described by Calvert and Pitts.[17]

Spin Orbit Coupling.—Irradiation of a 10^{-4} *M* solution of **1b** in cyclohexane showed a decreased rate of reaction from that of the nonbrominated material, **1a** (see Table I).[6] In order to determine the nature of this rate retardation as a spin orbit effect,[5] a cyclohexane solution of 13 ml of 1.08×10^{-4} *M* **1a** and 1 ml of ethyl bromide was irradiated in reference to a sample of 10^{-4} *M* **1a** in cyclohexane without ethyl bromide. An observed rate decrease in the former solution seemed to establish the intermolecular spin orbit effect.[4]

Registry No.—**1a**, 1969-74-0; **2a**, 1022-46-4.

Acknowledgment.—One of us (D. R. E.) wishes to express his indebtedness to Professor O. L. Chapman for many helpful discussions.

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[16] M. V. Bhatt, *Chem. Ind.* (*London*), 1390 (1956).

[17] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 783.

A Facile Synthesis of New Heterocycles from Glutaraldehyde

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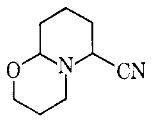
The reaction of glutaraldehyde dicyanohydrin with 3-aminopropanol to give the reduced pyrido[2,1-*b*][1,3]-oxazine (**1**) has been reported.[1] The apparent resemblance of this reaction to the remarkable Robinson–Schöpf synthesis[2] of pseudopelletierine from methylamine, acetone dicarboxylic acid, and glutaraldehyde suggested the following extensions.



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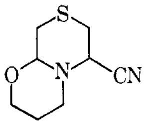
The reported procedure has been simplified and the yields improved by the use of a phosphate buffer and by the generation of the cyanohydrin *in situ* rather than in a separate step.[3] Thus an 80% yield of **1** is obtained when potassium cyanide (1.5 mol), glutaraldehyde (1.0 mol), and 3-aminopropanol (1.07 mol) are stirred in a phosphate buffer at pH 4 for 4 hr compared with 67% after 20 hr from the pure dicyanohydrin.[1] The reaction is pH sensitive and proceeds best between pH 3 and 7, only resinous products being formed at high pH. This pH dependence has also been reported for the synthesis of pseudopelletierine[4] and suggests that both reactions share a Mannich-like mechanism.

The following heterocycles were prepared by this simplified procedure.



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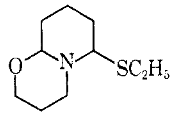

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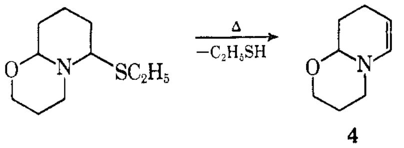
Compound **2**, a new ring system, was prepared in 45% overall yield from thiodiacetaldehyde diethylacetal.[5] Replacement of potassium cyanide in the synthesis by ethanethiol gave the product **3** in 88% yield. Although this product is thermally unstable and fails to give crystalline products with hydrochloric, perchloric, or picric acids, a concentrate with the proper ir spectrum was obtained. The ir spectrum of the distillation product showed a band at 1630 cm^{-1} which indicated that the enamine **4** had been formed. All attempts to characterize this labile enamine failed. Attempts to prepare more stable products by using diethyl malonate or ethyl cyanoacetate with glutaraldehyde and 3-aminopropanol in aqueous alcoholic solution instead of cyanide led only to intractable gums. As expected, amines (ammonia, benzylamine) and succinimide failed to give the corresponding bicyclic 1,1-diamine derivatives. An unusual 1,1-diamine, **5**, was, however, prepared by sub-



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[3] H. E. Johnson and D. G. Crosby, *J. Org. Chem.*, **27**, 1298 (1962).

[4] A. C. Cope, H. L. Dryden, C. G. Overberger, and A. A. D'Addieco, *J. Amer. Chem. Soc.*, **73**, 3416 (1951).

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