°C (methanol–water); IR 1530, 1520, 1490 cm^{-1}; UV 220 nm (end, ϵ 17 000), 229 (sh, 13 750), 252 (min, 750), 281 (sh, 7000), 285 (7750), 291 (sh, 7250); NMR δ 6.81 (s, 1 H), 6.65 (s, 2 H), 6.62 (s, 1 H), 4.2 (d, J = 16 Hz, 1 H, C-8H), 3.90 (s, 3 H), 3.78 (s, 3 H), 3.63 (s, 6 H), 2.50–3.83 (m, 8 H).

Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94. Found: C, 71.04; H, 7.03; N, 3.79.

Acknowledgments. I would like to thank Mike Woodman of Analytical Services and Methods, Searle Laboratories, for separating enamide *E–Z* isomers via low-pressure liquid chromatography, and Dr. Fred Hershenson, Searle Laboratories, for a gift of homopiperonylamine hydrochloride.

Registry No.—**3,** 61348-93-4; **4,** 61348-94-5; **5,** 61348-95-6; **6,** 61348-96-7; **7,** 61348-97-8; **8,** 61348-98-9; **9,** 61348-99-0; **10,** 61349-00-6; **11,** 61349-01-7; **12,** 61349-02-8; **13,** 19716-68-8; **14,** 10211-02-6; **15,** 61349-03-9; **16,** 36295-41-7; **17,** 61349-04-0; **18,** 61349-05-1; **19,** 61349-06-2; **20,** 61349-07-3; **21,** 61349-08-4; **22,** 483-49-8; **25,** 7259-08-7; **26,** 16724-64-4; **27,** 61349-09-5; **28,** 61349-10-8; 1-benzyl-3,4-dihydroisoquinoline, 24853-83-6; dihydropapaverine, 6957-27-3; 1-(3′,4′-methylenedioxybenzyl)-3,4-dihydro-6,7-dimethoxyisoquinoline HCl, 42971-28-8; 1-(3′,4′-methylenedioxybenzyl)-3,4-dihydro-6,7-methylenedioxyisoquinoline, 36295-45-1; 1-(3′,4′,5′-trimethoxybenzyl)-3,4-dihydro-6,7-dimethoxyisoquinoline, 61349-11-9; 1-(3′,4′,5′-trimethoxybenzyl)-3,4-dihydro-6,7-methylenedioxyisoquinoline, 61349-12-0; *N*-(3,4-dimethoxyphenylethyl)-2,5-dimethoxyphenylacetamide, 61349-13-1; 1-(2′,5′-dimethoxybenzyl)-3,4-dihydro-6,7-dimethoxyisoquinoline, 52050-48-3; 3,4-dihydro-6,7-dimethoxy-1-methylisoquinoline, 4721-98-6; 2,4-dimethoxybenzoyl chloride, 39828-35-8.

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Stilbenelike Photocyclizations of 1-Phenylvinyl-2-pyridones. Preparation of 4*H*-Benzo[*a*]quinolizin-4-ones[1]

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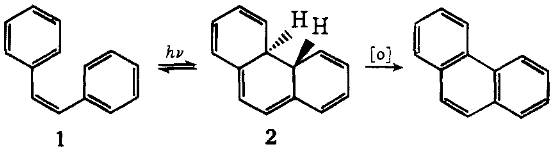
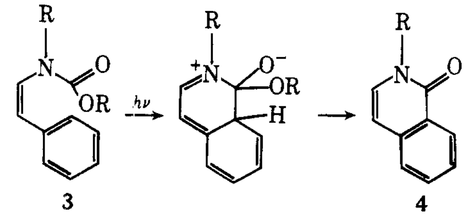
The photochemistry of 1-(2-phenylvinyl)-2-pyridone (**9**) and 1-(2,2-diphenylvinyl)-2-pyridone (**10**) has been investigated. Direct irradiation of **9** in a variety of solvents causes cis–trans photoisomerization exclusively. However, when irradiations are conducted on solutions of **9** containing hydrochloric acid with or without added iodine or oxygen, photocyclization occurs yielding 4*H*-benzo[*a*]quinolizin-4-one (**11**). Similarly, **10** is transformed to 4*H*-benzo[*a*]-7-phenylquinolizin-4-one by irradiation in solutions containing hydrochloric acid and no added oxidant. The mechanisms and regioselectivities of these reactions are discussed and compared to related observations from the photochemistry of acylaminostyrenes and aroylenamides.

Conjugated polyenes containing the hexatriene chromophore typically undergo photochemical electrocyclization reactions leading to products having the cyclohexadiene structural unit.[3] Characteristic of this reaction type are the facile conversions of *cis*-stilbenes (**1**) to dihydrophenanthrenes (**2**), which under oxidative conditions are transformed to phenanthrenes.[4] The striking synthetic potential of this general reaction has been repeatedly demonstrated and a large number of examples of its use in the synthesis of alkaloids[5] and heterocyclic compounds[6] have been presented.



1 **2**

Two interesting aspects of this reaction among many warrant comment owing to their relationship to the studies described below. Yang[5a,b] and Cava[5d] have shown, independently, that heterocyclic stilbene analogues possessing the acylaminostyrene **3** and aroylenamide **5** chromophores undergo photocylization reactions in a fashion similar to stilbene systems to produce the pyridones **4** and **6**, respectively.[7] An important feature of reactions of enamides which possess the potential for both stilbenelike and amidelike cyclizations, e.g., the carbamate **7**, has been noted.[5d] In these cases the product distributions appear to be dependent upon the presence or absence of an oxidant in the reaction medium. Since the dihydrophenanthrene intermediates resulting from the stilbene moiety reacting can revert to starting material in the absence of competing oxidative aromatization, amide cyclization pathways leading to pyridone products via nonoxidative alcohol eliminations predominate when irradiations are conducted on degassed solutions. In a similar vein, the directionality of stilbenelike photocyclizations is controlled by ortho substituents which participate in nonoxidative elimination reactions which irreversibly convert dihydrophenanthrene intermediates of general structure **8** to aromatic products.[5h,6e,8]



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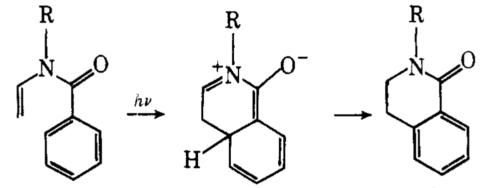

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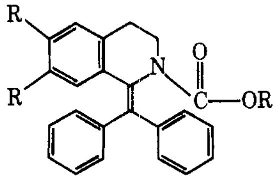

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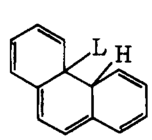

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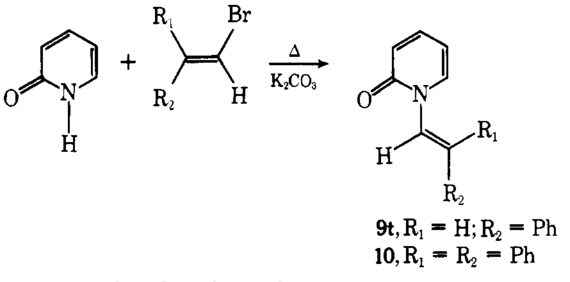
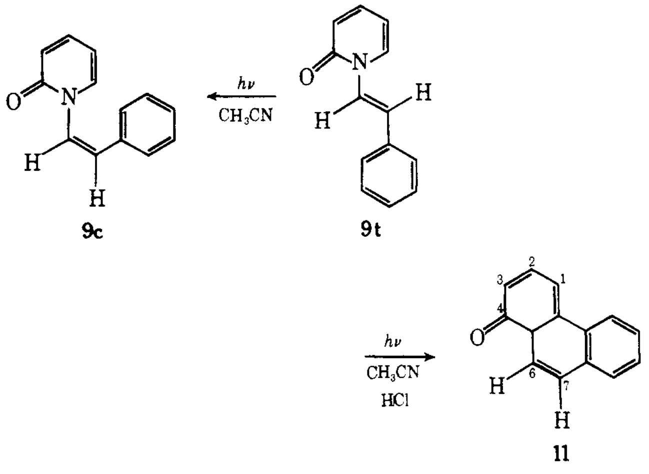
Results from our recent exploratory photochemical studies of two heterocyclic stilbene analogues, 1-(2-*trans*-phenylvinyl)-2-pyridone (**9t**) and 1-(2,2-diphenylvinyl)-2-pyridone (**10**), appear related to these observations. Both compounds are easily prepared by reaction of 2-pyridone with the corresponding vinyl bromide in the presence of potassium carbonate. Irradiation (flint glass, 9.2 mM) of the *trans*-styrylpyridone **9t** in a variety of solvents (acetonitrile, ethanol, or benzene) led exclusively to cis–trans isomerization and production of the *cis*-styryl isomer, **9c** (R^1 = H; R^2 = Ph). Irradiations for extended periods (12 h) using these conditions which allow for light absorption by the *cis*-styrylpyridones (see UV absorption properties of **9c** in Experimental Section) failed to produce detectable quantities of additional products. Contrastingly different results were obtained when acetonitrile or ethanol solutions of **9t** containing added hydrochloric acid were irradiated. Under these conditions the styrylpyridone was slowly converted (2%, 7 h irradiation, Vycor) to 4*H*-benzo[*a*]quinolizin-4-one (**11**). A substantial increase in the yield of **11** was noted when photolysis of **9t** was conducted on air-saturated solutions containing iodine and using unfiltered light.



9t, R_1 = H; R_2 = Ph
10, R_1 = R_2 = Ph

The structure of the quinolizinone product of these reactions was determined initially using spectral data. Exceptionally informative was the ultraviolet–visible spectrum of **11**, which displayed characteristic structured bands with maxima extending to 410 nm. In addition, the ^{1}H NMR having an AB quartet for the H-6 and H-7 protons and an H-6 chemical shift of 8.91 ppm resulting from its rigid location in the carbonyl and aromatic deshielding regions seemed consistent with structure **11**. Firm support for this assignment derived from the reaction sequence shown below in which **11** was converted to the known benzo[*a*]quinolizinium perchlorate[9] **13**, via the chloroquinolizinium chloride **12**. The spectral and physical properties of the derived perchlorate were identical with those of the known salt obtained by photocyclization of *N*-styrylpyridinium chloride followed by perchlorate ion exchange.[6a-c]



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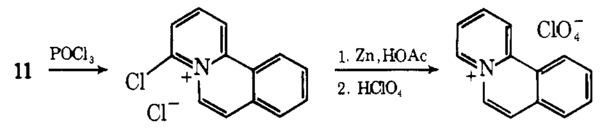
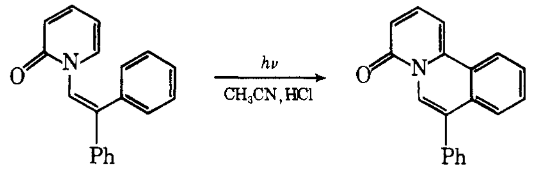


12 **13**

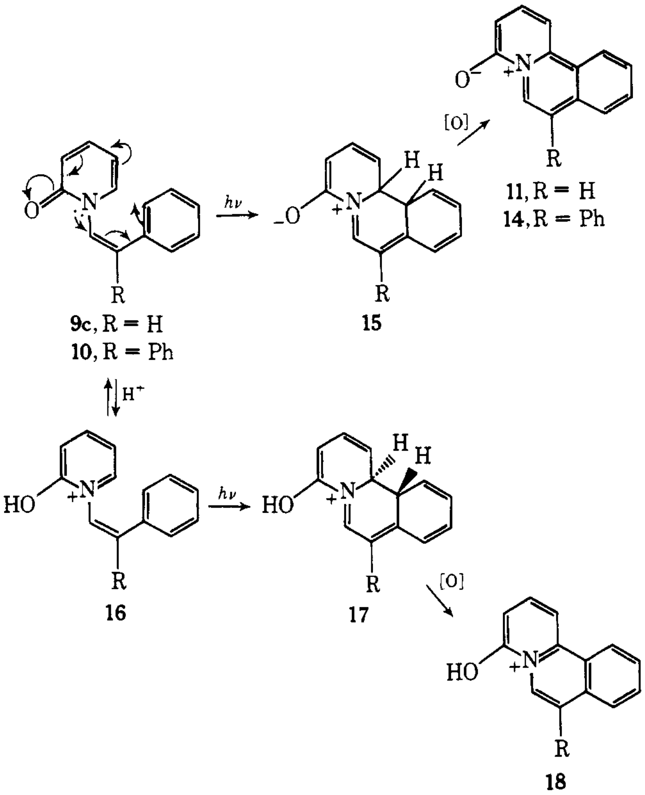
Similar results were obtained when the diphenylvinyl-2-pyridone **10** was irradiated in acetonitrile solutions containing hydrochloric acid. The sole product (60%) generated under these reaction conditions was found to be 4*H*-benzo[*a*]-7-phenylquinolizin-4-one (**14**), the structure of which rests solidly on accumulated spectral data. Here, as in the case of the styrylpyridone photolyses, irradiations in the absence of acid failed to generate cyclization products. It is also important to mention at this point that both the *cis*-styryl and diphenylvinyl pyridones, **9c** and **10**, do not lead to **11** and **14**,



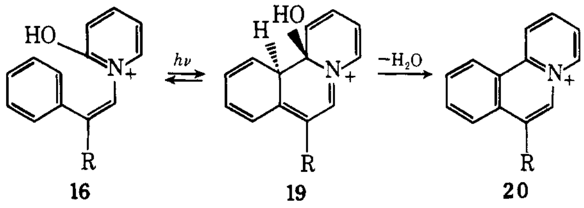
10 **14**

respectively, under dark reaction conditions identical with those used in successful photochemical runs.

Several features of the stilbenelike photocyclization reactions of the *N*-styryl-2-pyridones **9** and **10** beyond their obvious utility in the preparation of benzoquinolizin-4-one systems require a more detailed discussion. First, the mechanism for transformation of these heterocyclic stilbene analogues can be envisaged as paralleling in part those offered to rationalize similar photoreactions of acylaminostyrenes[5a,b,d] and *N*-styrylpyridinium salts.[9] Accordingly, the excited pyridones, **9c** and **10**, behaving as vinologous acylaminostyrenes, can cyclize to produce the intermediate zwitterions **15** which would then proceed to the quinolizinone products by oxidative dehydrogenation. Alternatively and perhaps more appropriately considering the condition used for photolysis, the hydroxypyridinium salts **16**, formed by reversible protonation of the pyridone reactants, can undergo cyclization upon direct irradiation to produce the dihydrobenzoquinolizinium salts **17**. Oxidation of **17** followed by deprotonation would lead to the observed products.[10] The latter mechanism appears to be more in accord with our observations. As noted above, irradiations of acetonitrile or ethanol solutions of **9t** and **10** for extended periods failed to cause formation of detectable quantities of **11** and **14**. In contrast, efficient photocyclizations of these materials occurred when hydrochloric acid was present in the reaction medium. In addition, on the basis of estimated pK_a values for N-substituted hydroxypyridinium salts, e.g., 0.32 for 1-methyl-2-hydroxypyridinium iodide,[11] one can predict that modestly high percentages of the pyridones **9c** and **10** should exist in their protonated forms. Indeed ultraviolet spectra of these compounds in solutions containing greater than 7×10^{-2} M HCl display maxima at 285 and 288 nm, respectively, characteristic of hydroxypyridinium salts and not the neutral pyridones which absorb maximally at 339 and 323 nm in neutral solutions.



A second aspect of these observations is the selectivity displayed in photocyclization of both **9** and **10**. A priori, two cyclization pathways are available to the excited hydroxypyridinium salts **16**, one leading to the protonated dihydroquinolizinium salts **17** and another generating the structurally isomeric salts **19**. It is surprising that this latter excited state reaction pathway producing eventually **20** is not adhered to when reactions are conducted in the presence of acid but in the absence of added oxidizing agent even though nonoxidative irreversible dehydration of the intermediate **19** is possible. Thus, it appears that the regiochemistry of protonated phenylvinyl-2-pyridone photocyclizations is evidently not controlled by factors similar to those operable in related reactions of *N*-acylaminostyrene and stilbene systems. Reasons for this divergent behavior displayed by closely related compounds are not obvious but may be related to electron densities at C-6 and C-2 in the excited hydroxypyridinium moiety or conformational preferences about the styryl–pyridyl bond. These have not yet been subjected to experimental scrutiny. In any event, the photochemistry of 1-phenylvinyl-2-pyridones has yielded novel examples of a well-studied reaction type and has provided an efficient method for preparation of an interesting class of heterocyclic compounds.



Experimental Section

Melting points are reported uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. NMR spectra were recorded on Varian HA-100 and T-60 (proton) and JEOL PS-100 (carbon) spectrometers with tetramethylsilane as the internal standard. Infrared spectra were recorded on Beckman IR-8 and Perkin-Elmer 237 spectrophotometers. Ultraviolet and visible spectra were recorded using a Beckman Acta-III spectrophotometer. High-resolution mass spectral data were obtained using a CEC-21-110 double-focusing mass spectrometer.

1-(2-*trans*-Phenylvinyl)-2-pyridone (9t). A solution containing 1.00 g (0.011 mol) of 2-pyridone, 1.93 g (0.011 mol) of *trans*-β-bromostyrene, and 3.00 g (0.022 mol) of anhydrous potassium carbonate in 20 ml of anhydrous dimethylformamide was refluxed for 18 h under nitrogen. After cooling to room temperature the reaction mixture was poured into ice water. The solid precipitate formed was filtered, dried, and recrystallized (absolute ethanol), giving 1.95 g (94%) of pure 1-(2-*trans*-phenylvinyl)-2-pyridone as a light yellow solid, mp 147.5–150 °C. Spectral properties of this material follow: ^{1}H NMR ($CDCl_3$) δ 6.21 (t, 1 H, H-5), 6.57 (dm, 1 H, H-3), 6.65 (d, 1 H, J = 15 Hz, H-2′), 7.55 (m, 6 H, H-4 and phenyl), 7.58 (dm, 1 H, H-6), and 7.97 (d, 1 H, J = 15 Hz, H-1′); ^{13}C NMR ($CDCl_3$) δ 161.2 (s, C-2), 120.9 (d, C-3), 132.6 (d, C-4), 106.6 (d, C-5), 139.3 (d, C-6), 128.0 (d, C-1′), 121.2 (d, C-2′), 134.6 (s, phenyl C-1), 126.5 (d, phenyl C-2), 128.7 (d, phenyl C-3), 125.7 (d, phenyl C-4); UV (95% ethanol) max 339 nm (ε 13 000); IR (KBr) 1653, 1585, 1524, 765, 753, and 692 cm^{-1}.

Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.09; H, 5.55; N, 7.12.

1-(2,2-Diphenylvinyl)-2-pyridone (10). A neat solution of 2-hydroxypyridine (5.00 g, 0.053 mol) in 13.50 g (0.053 mol) of 1,1-diphenyl-2-bromoethylene containing 14.50 g (0.105 mol) of suspended anhydrous potassium carbonate at 160 °C was stirred for 48 h under nitrogen. A solution of the resulting viscous brown oil in chloroform was washed with water, dried, and concentrated in vacuo, giving 13.60 g of a brown oil which was subjected to column chromatography on silica gel (Davison grade 950, 60–200 mesh). Elution with 10–100% ether–hexane gave 2.00 g of recovered unreacted bromide and pyridone. Elution with 10% chloroform–ether gave 9.80 g of a brown solid containing the desired diphenylvinylpyridone. Recrystallization from benzene gave 8.80 g (62%) of pure 1-(2,2-diphenylvinyl)-2-pyridone, mp 148–150.5 °C. Spectral properties of this material follow: ^{1}H NMR ($CDCl_3$) δ 5.55 (t, 1 H, J = 3 Hz, H-5), 6.51 (dm, 1 H, J = 4 Hz, H-3), 6.90 (dm, 1 H, J = 3 Hz, H-4), 7.20 (m, 12 H, H-6, H-1′, and phenyl); ^{13}C NMR ($CDCl_3$) δ 163.1 (s, C-2), 120.8 (d, C-3), 137.5 (d, C-4), 105.4 (d, C-5), 139.7 (d, C-6), 130.0 (C-1′), 125.2 (d, C-2′), 139.3, 128.8, 136.7, 128.3 (phenyls); UV (absolute ethanol) max 323 nm (ε 10 300); IR ($CHCl_3$) 1675, 1600, 1650 cm^{-1}.

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.42; H, 5.51; N, 5.00.

1-(2-*cis*-Phenylvinyl)-2-pyridone (9c). A solution of 1-(2-*trans*-phenylvinyl)-2-pyridone (1.082 g, 5.49 mmol) in 600 ml of degassed acetonitrile was irradiated in a preparative apparatus (quartz, water-cooled immersion well housing a 450-W Hanovia medium-pressure lamp and flint glass filter and immersed in an outer flask) under nitrogen. The disappearance of *trans*-styrylpyridone was monitored by UV spectral changes on removed and diluted aliquots. After a sufficient quantity of starting material was consumed (1.0 h), irradiation was terminated and the photolysate concentrated in vacuo, giving an oil which was subjected to column chromatography on Florisil (Fisher, 100–200 mesh). Elution with chloroform gave pure 1-(2-*cis*-phenylvinyl)-2-pyridone (0.303 g, 28%) as a yellow oil. Spectral properties of this material follow: ^{1}H NMR ($CDCl_3$) δ 5.98 (t, 1 H, H-5), 6.51 (d, 1 H, J = 10 Hz, H-2′), 6.63 (d, 1 H, H-3), 6.97 (d, 1 H, J = 10 Hz, H-1′), 7.10 (t, 1 H, H-4), 7.22 (m, 5 H, phenyl), 7.35 (d, 1 H, H-6); ^{13}C NMR ($CDCl_3$) δ 162.4 (s, C-2), 121.3 (d, C-3), 137.3 (d, C-4), 106.1 (d, C-5), 140.2 (d, C-6), 128.2 (d, C-1′), 125.0 (d, C-2′), 132.8 (s, phenyl C-1), 128.7 (d, phenyl C-2 and C-3), 127.2 (d, phenyl C-4); UV (95% ethanol) max 224 nm (ϵ 14 000), max 252 (7160), max 315 (7180); IR (liquid film) 1727, 1650, 1577, 1527, 1140, 772, 752, and 698 cm^{-1}; high-resolution mass spectrum, parent ion, calcd for $C_{13}H_{11}NO$, 197.0841; found experimentally, 197.0850.

4*H*-Benzo[*a*]quinolizin-4-one (11). A solution containing 8.600 g (0.044 mol) of 1-(2-*trans*-phenylvinyl)-2-pyridone and 0.10 g (0.80 mmol) of iodine in 2000 ml of 95% ethanol (or acetonitrile) and 50 ml of concentrated hydrochloric acid was irradiated using the preparative apparatus described above with unfiltered light for 23 h. During the course of irradiation oxygen was bubbled through the solution and one additional 0.10-g portion of iodine was added. The crude photolysate was concentrated in vacuo, giving 10.1 g of a black solid which was dissolved in chloroform and washed with saturated potassium carbonate and saturated sodium bisulfite solutions. The chloroform layer was dried and concentrated in vacuo, giving 6.50 g of a red oil whose NMR showed it to contain ca. 50% of the desired quinolizinone (crude yield ca. 37%). This oil was repeatedly extracted with ether and the ethereal solution obtained gave upon concentration in vacuo 2.11 g (24.5%) of pure 4*H*-benzo[*a*]quinolizin-4-one as a yellow-tan solid, mp 132.5–134.5 °C. This material is extremely sensitive in its pure form to both light and oxygen.

The spectral properties of this compound follow: ^{1}H NMR ($CDCl_3$) δ 6.74 (d, 1 H, H-3), 7.08 (d, 1 H, J = 8.0 Hz, H-7), 7.35 (d, 1 H, H-1), 7.64 (m, 4 H, aryl), 8.29 (t, 1 H, H-2), 8.91 (d, 1 H, J = 8.0 Hz, H-6); ^{13}C NMR ($CDCl_3$) δ 128.2 (d, C-1), 130.3 (d, C-2), 159.3 (s, C-4), 137.8 (d, C-6), 126.8 (d, C-7), 126.0 (s, C-7a), 130.1 (s, C-11a), 140.5 (s, C-11b), 99.2, 114.3, 126.8, 123.4, 112.3 (for C-3, C-8, C-9, C-10, C-11); UV (95% ethanol) max 220 nm (ϵ 22 800), 228 (28 000), 235 (32 100), 257 (8160), 256 (9800), 290 (10 900), 300 (17 800), 370 (9450), 388 (15 900), 410 (15 700); IR (KBr) 1658, 756, 647 cm^{-1}; high-resolution mass spectrum, parent ion calcd for $C_{13}H_9NO$, 195.0684; found experimentally, 195.0681.

Benzo[*a*]quinolizinium Perchlorate (13). 4*H*-Benzo[*a*]quinolizin-4-one obtained from the photolysis above (0.900 g, 4.60 mmol) was mixed with 30 ml of phosphorus oxychloride and the resulting solution heated at reflux for 30 min. The resulting solution was concentrated in vacuo, giving an oil which was dissolved in 100 ml of glacial acetic acid containing 3.00 g (0.046 mol) of powdered zinc. After stirring at reflux for 30 min, the hot solution was filtered through Celite. The filtrate was diluted with water and concentrated in vacuo, giving a residue which was dissolved in 100 ml of 70% perchloric acid. Upon dilution of this solution with water and cooling to −10 °C, 0.852 g (75.5%) of benzo[*a*]quinolizinium perchlorate crystallized as yellow needles, mp 197.0–197.5 °C (lit.[9] 197 °C). All spectral properties of the perchlorate salt prepared in this fashion were identical with those measured on material by photocyclization of 1-(2-phenylvinyl)pyridinium chloride followed by perchlorate ion exchange.

4*H*-Benzo[*a*]-7-phenylquinolizin-4-one (14). A solution containing 0.500 g (1.83 mmol) of 1-(2,2-diphenylvinyl)-2-pyridone in 1000 ml of degassed 0.5% hydrochloric acid in acetonitrile was irradiated using the preparative apparatus described above with a vycor filter for 30 min. The cloudy photolysate was concentrated in vacuo, giving a highly phosphorescent yellow solid which was subjected to TLC on 20 × 20 cm plated with silica gel (Merck, GF-254) as absorbant. Elution with 20% benzene–chloroform gave unreacted starting material (R_f 0.9, 0.182 g, 36%) and pure 4*H*-benzo[*a*]-7-phenylquinolizin-4-one (R_f 0.35, 0.293 g, 60%) as a light- and air-sensitive gold solid. The instability of this material prevented determining its melting point.

The spectral properties of this compound follow: ^{1}H NMR ($CDCl_3$) δ 6.70 (d, 1 H, J = 4 Hz, H-3), 7.45 (m, 10 H, phenyl, aryl, and H-1), 8.28 (t, 1 H, J = 1 Hz, H-2), 8.80 (s, 1 H, H-6); ^{13}C NMR ($CDCl_3$) δ 128.7 (d, C-1), 130.5 (d, C-2), 99.2 (d, C-3), 159.7 (s, C-4), 136.0 (C-6), 139.7 (s, C-7), 127.7 (s, C-7a), 130.1 (s, C-11a), 140.7 (s, C-11b), 112.8, 128.3, 125.9, 122.3, 138.1, 124.2 (for phenyl, C-8, C-9, C-10, C-11); UV (absolute ethanol) max 301 nm (ϵ 16 400) and 227 (56 300); IR ($CHCl_3$) 1670, 1525, and 1230 cm^{-1}; high-resolution mass spectrum, parent ion calcd for $C_{19}H_{13}NO$; 271.0997; found experimentally, 271.1001.

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Registry No.—**9t,** 61259-55-0; **9c,** 61259-56-1; **10,** 61259-57-2; **11,** 61259-58-3; **13,** 4146-32-1; **14,** 61259-59-4; 2-pyridone, 142-08-5; *trans*-β-bromostyrenes, 588-72-7; 2-hydroxypyridine, 109-10-4; 1,1-diphenyl-2-bromoethylene, 13249-58-6; perchloric acid, 7601-90-3.

References and Notes

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