

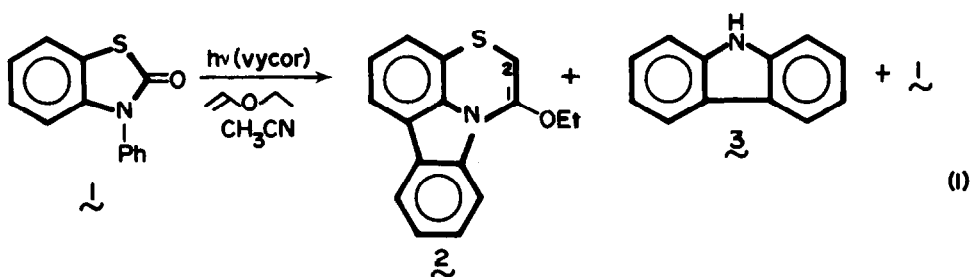
A NEW PHOTOREACTION OF N-PHENYL-2-BENZOTHAZOLINONE WHICH PRODUCES
THE PREVIOUSLY UNREPORTED [1,4]-THIAZINO[2,3,4-jk]CARBAZOLE SYSTEM.

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As part of a search for photoreactions which might serve as key steps in heterocyclic synthesis, we have explored the photochemistry of N-phenyl-2-benzothiazolinone (**1**). The possible generation of a trappable ortho quinoid intermediate by the extrusion of CO from **1** was envisioned. Ortho quinoid intermediates could be useful for the preparation of new phenothiazine and benzothiazine compounds which are known to exhibit antipsychotic^{1a} and antiinflammatory activity, respectively. The observed photoreactivity of **1** in the presence of the electron rich dienophile, ethyl vinyl ether, is more complex than expected and leads to the previously unreported [1,4]thiazino[2,3,4-jk]carbazole ring system **2** shown in equation (1).



A solution of N-phenyl-2-benzothiazolinone (**1**)² (100 mg, 0.37 mmol) and ethyl vinyl ether (13.8 g, 192 mmol) in 150 mL of acetonitrile was purged with argon and irradiated (450 W Hanovia, medium press.lamp) through vycor for 2 hr. The resulting yellow suspension was concentrated at reduced pressure (<40°C) and chromatographed on a florisil column (100 g). Dichloromethane eluted carbazole (**3**) (6.2 mg, 8.4%), which was identical with authentic material, and a new compound (37 mg, 31%) with mp 93.0-94.0°C (uncorr) which analyzed correctly for $\text{C}_{16}\text{H}_{15}\text{NOS}$. Further

elution of the column with dichloromethane-methanol gave 19.4 mg (19.4%) of recovered λ .

The spectral data of the new compound are consistent with the structure shown for λ , 1-ethoxy-1,2-dihydro-[1,4]thiazino[2,3,4-jk]carbazole: ^1H NMR (CDCl_3) δ 1.15 (t, 3H, $J=7\text{Hz}$), 3.15 (t, 2H, $J=3\text{Hz}$), 3.3-3.9 (m, 2H), 5.9 (t, 1H, $J=3\text{Hz}$), 6.9-8.0 (m, 7H); ^{13}C NMR (CDCl_3)³ δ 15.01 (q), 31.03 (t), 63.89 (t), 76.73 (d), 108.66, 116.69, 120.13, 120.31, 120.80, 122.26, 122.66, 125.89, 126.23, 133.23, 140.21; IR (CHCl_3) 1600, 1575, 1490, 1450, 1430, 1380, 1340, 1325, 1185, 1130, 1095, and 1070 cm^{-1} ; and mass spectrum m/e (rel. intensity) 269 (15), 224 (22), 167 (100), 86 (59), and 84 (93). The infrared peaks are present at frequencies nearly identical with those of carbazole systems, and the ^1H NMR spectrum shows an isolated ethyl group with diastereotopic methylene protons (m at δ 3.3-3.9), as well as coupled methine and methylene groups (the nonequivalent methylene protons appear as a pair of overlapped doublets at δ 3.15). The position of the ethoxy group was shown to be at C,1 rather than C,2 by comparison of off-resonance decoupled ^{13}C NMR spectra of λ and the sulfone produced by potassium permanganate oxidation of λ . The sulfone gave ^{13}C NMR (CDCl_3)³ signals at δ 14.77 (q), 53.23 (t), 64.59 (t), 80.88 (d), 109.80, 119.37, 120.34, 121.03, 121.28, 122.68, 122.86, 124.26, 124.57, 127.33, (IR, ^1H NMR, and mass spectra were as expected). Sulfur oxidation shifted the methylene carbon signal (not due to ethoxy) from δ 31.03 to δ 53.23 while the methine carbon (more distant from sulfur in the structure given for λ) was only shifted from δ 76.73 to δ 80.88 upon oxidation.

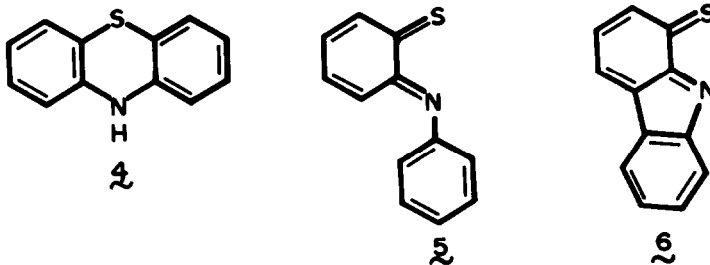
The reaction does not give analogs of λ when cyclohexene or acrylonitrile are used in place of ethyl vinyl ether. The use of ketene diethyl acetal, an electron rich dienophile which might have given the amide or thiol lactone, resulted in an unidentifiable complex mixture.

The mechanism of the reaction (including the required oxidation step) has not been determined, but must be consistent with the following experimental information: 1) photolysis of λ in the absence of dienophile trap and in the presence of alkenes which do not give products analogous to λ gives carbazole, recovered λ , and some intractable material; 2) the trapping of ethyl vinyl ether is completely regioselective within experimental error; and 3) the photoreaction to yield λ was neither quenched by piperylene nor sensitized by acetone; however, the formation of carbazole was quenched by piperylene and sensitized by acetone.

Thermally (750°C) λ is known⁴ to give carbazole via a phenothiazine (λ) intermediate.

Phenothiazine has not been observed in any photolysis of λ . However, we cannot rule out the presence of λ during photolysis of λ , since we have found λ to be photolabile under these conditions. It is unlikely that λ is an intermediate leading to λ or λ since its photolysis with or without added ethyl vinyl ether does not give these products. The quenching and sensitizing results indicate that a common intermediate could not lead to both λ and λ .

The nature of the intermediate ground or excited state species intercepted by ethyl vinyl ether to form λ is unclear. Ortho quinoid λ has been postulated to rationalize the formation



of λ upon thermolysis of λ , and it could be important photochemically if the proposed rearrangement to λ is slow enough at room temperature to allow trapping. Another trappable intermediate, λ , could lead to λ , but not to λ .

Carbazole (λ) is evidently formed from λ by a triplet reaction, and this is consistent (perhaps coincidentally) with reported photochemical carbazole formation from diphenyl amines.⁵ The reaction may involve expulsion of OCS from the triplet state (as compared to expulsion of CO from the singlet state).

We are continuing to study the generality of this photoreaction of λ and other readily synthesized N-substituted 2-benzothiazolinones.

Acknowledgments

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