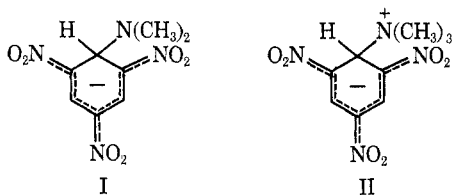


low. The shape should not be affected drastically by this possible error, however. Thus there can be no doubt that the general character of the spectrum of XH is definitely different from that of X⁻; for obvious reasons we do not attach importance to the lower extinction coefficient at the absorption maximum. (3) It is interesting that the effect of attaching a proton to the amine nitrogen on X⁻ brings about a bathochromic shift of *ca.* 13 m μ . An analogous creation of a positive charge through addition of a methyl or ethyl group either does not change the absorption maximum or shifts it slightly to *shorter* wavelengths, as seen by comparing I and II^{5a} or the ethyl analog.² This may



be related to the capability of forming an intramolecular hydrogen bond to the *ortho* nitro group in the present case and the lack of this possibility when the nitrogen bears three alkyl groups. Other evidence for such intramolecular hydrogen bonding has been discussed.¹ (4) The fact that the calculation of spectra based on complex concentrations derived from kinetic equilibrium data gives satisfactory extinction coefficients shows convincingly that Y⁻ and YH do not significantly absorb in the visible, an observation which had been used as partial evidence in assigning the structure of YH and Y⁻.¹ However, the experimental uncertainties in this system are too large to allow complete exclusion of the possibility of a fourth interaction of CT¹¹-complex formation.⁴ If a fourth complex were formed with a small equilibrium constant, an additional term would need to be added to *D* in eq 2-4; if it were small enough (*e.g.*, *ca.* 0.5 l. M⁻¹ as in acetonitrile⁴) so as not to alter *D* significantly, it would escape unnoticed.

Registry No.—Piperidine-TNB complex (XH), 12402-43-6; piperidine-TNB complex (X⁻), 12402-42-5; 1,3,5-trinitrobenzene, 99-35-4.

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(11) Charge transfer.

1,2 Cycloaddition of Singlet Oxygen to 9,9'-Bifluorenylidene

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Typically the reactions of singlet oxygen with olefins has been studied with olefins possessing allylic hydrogen atoms.¹ The resulting allylic hydroperoxides were

suggested to arise by an "ene"-type mechanism.² In contrast, there are few reports of 1,2 cycloadditions of singlet oxygen to olefins. Cycloaddition of singlet oxygen to olefins is suggested when nitrogen is conjugated with the olefinic site. Thus, enamines^{1a,3} and 10,10'-dimethyl-9,9'-biacridylidene⁴ undergo cleavage of the double bond with singlet oxygen, a result expected from decomposition of the 1,2-dioxetane intermediate produced by cycloaddition. It can be noted that tetra-aminoethylenes give analogous products, ureas, with ground-state triplet oxygen.⁵ Recently, cycloaddition of singlet oxygen to indene and methylated indenenes was demonstrated⁶ even though allylic hydrogen atoms were present. This is to be contrasted with the lack of reaction of norbornene with singlet oxygen.¹⁶ The bridgehead location of the allylic hydrogens voids the "ene"-type reaction which would lead to a bridgehead double bond, but the possibility of 1,2 cycloaddition exists. We report here some of our results in the search for 1,2 cycloaddition of singlet oxygen to olefins.

Our interest in 1,2-dioxetane intermediates⁷ led us to investigate the possible intervention of this intermediate in the reaction of singlet oxygen with an olefin devoid of allylic hydrogens and heteroatoms. For this purpose we chose to study the reaction of 9,9'-bifluorenylidene (I) with singlet oxygen, which is generated both chemically and photochemically. A 1,2-dioxetane intermediate, resulting from a cycloaddition reaction between I and singlet oxygen, will give fluorenone by analogy to the decomposition of other such intermediates.^{7,8}

Singlet oxygen was generated chemically from hydrogen peroxide and sodium hypochlorite⁹ as well as photochemically from oxygen with methylene blue sensitizer.^{9b} Competitive oxidations with mixtures of I and 2-methyl-2-butene (II) were carried out. Chemical generation of singlet oxidation gave fluorenone in 44% yield from I and 41% reaction of II. Fluorenone was isolated and characterized from a reaction where II was excluded. Photosensitized oxidation of the olefin mixture gave fluorenone in 91% yield along with 66% reaction of II. To verify that fluorenone was generated from singlet oxygen, which in turn was produced from the sensitizer, a control reaction was carried out under the conditions of the sensitized oxygenation, but without the sensitizer. The yield of fluorenone was reduced

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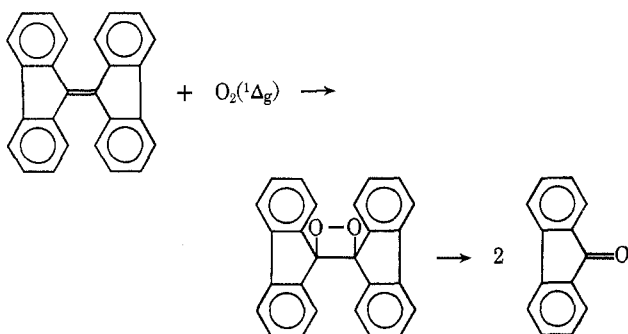
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to 0.2%. The ratio of per cent reaction of I/II in the chemical and photochemical reaction is 1.1 and 1.4, respectively. The similarity of these two ratios suggest that singlet oxygen is the oxidant.^{1a,d} Foote^{1a} has presented relative reactivities for a series of olefins with singlet oxygen. With II as the common olefin in this series and the present data, I may be placed in the series. It is found that I is 0.034 times as reactive with singlet oxygen as tetramethylethylene, which is the most reactive monoolefin in the series. However, I is 720 times as reactive as *trans*-4-methyl-2-pentene, the least reactive olefin. The results indicate that allylic hydrogen atoms are not a prerequisite for facile reaction of singlet oxygen with an appropriately substituted olefin. The most reasonable mechanism for the reaction is *via* a 1,2-dioxetane intermediate as shown below.



The generation of the 1,2-dioxetane by methods previously employed by us⁷ and the initial electronic state of fluorenone are currently under investigation.

Experimental Section¹⁰

Materials.—9,9'-Bifluorenylidene (I) (Matheson Coleman and Bell), mp 193–194° (lit.¹¹ mp 188–190°), was used as received. The nmr spectrum of three multiplets centered at 7.12, 7.50, and 8.20 with relative areas of 2:1:1 was consistent with that previously reported.¹² The ir spectrum was void of significant absorption in the carbonyl region. The following chemicals were obtained from Matheson Coleman and Bell and were used without further purification: 2-methyl-2-butene (II), 30% hydrogen hydroperoxide, methylene blue chloride, and biphenyl. A 5% sodium hypochlorite (Purex) solution was used. The reagent grade solvents, methanol, dioxane, and methylene chloride, were used as received. Reagent grade tetrahydrofuran was distilled from calcium hydride.

Photosensitized Oxygenations.—An immersion photochemical reactor similar to the design given by Gollnick and Schenck¹³ was used with circulating ice-cooled water. Oxygen was passed in a slow stream through a glass frit in the bottom of the reactor. Irradiation was carried out with a Sylvania Type DWY-625W tungsten-iodine lamp operated at 60 V. In a typical reaction, the reactor was charged with 0.3304 g (1.00 mmol) of I, 70.2 mg (1.00 mmol) of II, 50 mg of methylene blue, and 133.5 g of methylene chloride. Photooxygenation was conducted for 2.33 hr. At this time an aliquot was removed and weighed. Biphenyl and tetrahydrofuran (THF) were weighed into the aliquot as standards for glpc analysis. The samples were kept cool and immediately subjected to glpc analysis. Analyses for II and the

(10) Gas-liquid partition chromatography (glpc) was performed on a Varian Aerograph Hy-F:III Series 1200 flame ionization instrument. Infrared spectra were measured in carbon tetrachloride with a Perkin-Elmer Model 621 spectrometer. Nmr spectra was determined in carbon tetrachloride solution with a Varian Model A-60 spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to internal tetramethylsilane as 0 ppm (δ scale). All melting points are corrected and were determined with a Hoover-Thomas capillary melting point apparatus.

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THF internal standard were carried out on a PAR-2, 5 ft \times $\frac{1}{8}$ in. column, operated at 103° (injector 220°, detector 250°) with a 29-ml/min flow of nitrogen. Retention times for a 1- μ l injection were 10 and 19 min, respectively, for I and THF. Analyses for fluorenone and the biphenyl internal standard were performed on a 15% Apiezon L on Chromosorb G, 10 ft \times $\frac{1}{8}$ in. column, operated at 220° (injector 220°, detector 250°) with a 29-ml/min flow of nitrogen. Retention times for a 1- μ l injection were 5.6 and 21 min, respectively, for biphenyl and fluorenone. Yields and per cent reaction, based on initial amounts of I and II, were calculated from the glpc data by comparison with standard mixtures of the solvent, II, fluorenone, and the internal standards. In one reaction with I, the methylene chloride solvent was removed on a rotary evaporator. The remaining mixture was triturated with ether and then filtered to remove methylene blue. The concentrated filtrate was subjected to column chromatography on Merck acid-washed alumina to give fluorenone, mp 82.5–83.5° (lit.¹⁴ mp 83°). Nmr and ir spectra of the sample were identical with those given in the Sadler spectra.

Oxygenation with Sodium Hypochlorite-Hydrogen Peroxide.—In a typical reaction, 15 ml of 5% Purex (0.67 M, 10 mmol) was added with mechanical stirring to an ice-cold solution of 0.3304 g (1.00 mmol) I, 74.6 mg (1.07 mmol) II, 2.1 ml of 30% hydrogen peroxide (9.4 M, 20 mmol), 20 ml of methanol, and 80 ml of dioxane. After a 7-min addition period, followed by stirring for 1 hr, an aliquot was withdrawn and subjected to glpc analysis for II as described in the previous section. Glpc analysis for fluorenone was carried out as described above, but after work-up by extracting with ether, drying over magnesium sulfate, and concentrating on a rotary evaporator. Fluorenone was identified in these reactions by comparison of glpc retention times and by thin layer chromatography.

Registry No.—I, 746-47-4; II, 513-35-9.

Acknowledgments.—This investigation was supported by the Petroleum Research Fund, Administered by the American Chemical Society.

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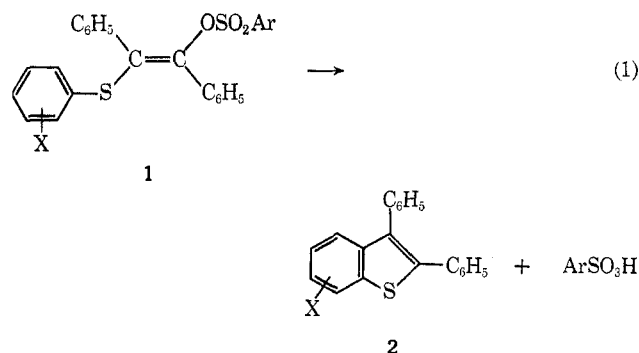
Cyclization of Arylthiovinyl Sulfonic Esters to Benzo[*b*]thiophenes. An Unusual 1,2-Sulfur Shift

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An unusual rearrangement was observed in the cyclization of some arylthiovinyl sulfonic esters **1** to benzo[*b*]thiophenes **2**¹ (eq 1).



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