Tetrahedron Letters No.56, pp. 5895-5898, 1968. Pergamon Press. Printed in Great Britain.

QUENCHING OF AN EXCITED SINGLET STATE OF 2-PHENYLTHIOPHENE

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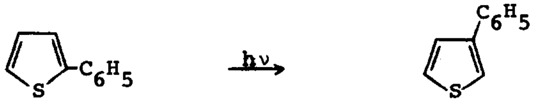
(Received in UK 30 September 1968; accepted for publication 18 October 1968)

We have investigated the effect of piperylene (1,3-pentadiene) on the irreversible photorearrangement of 2-phenylthiophene (I) to 3-phenylthiophene (II) (1,2). The experiments described below indicate that piperylene severely inhibits this rearrangement by means of efficient photochemical adduct formation between a singlet of I and ground state diene.



I II

A. 2-Phenylthiophene (I) disappears at 5 times its normal rate when irradiated in ether solution in the presence of piperylene. Only 1-2% of rearrangement product is formed (3). A plot of the reciprocal of the relative quantum yield of disappearance of I against the reciprocal of the piperylene concentration yields a straight line (4).

B. Evaporation of the solution described above (1 M in piperylene, 30% consumption of I) left an unstable oil. Immediate injection by means of a cold probe into the mass spectrometer (5) showed only one new product (formed qualitatively in good yield). This product corresponded to a 1:1 adduct of I and piperylene with a parent peak at 228 ($C_{15}H_{16}S$). Major cracking patterns for this material were at M-15 ($-CH_3$) and M-32 (-S) (6).

C. In the presence of piperylene (0.975 M) fluorescence of I was reduced to 58% of its original value.

In the concentration range of 0-1.3 M piperylene a plot of Φ_{f_o}/Φ_f for I (10^{-4} M) against piperylene concentration is cleanly linear with a slope of 0.77 M^{-1}. 1,3-Cyclohexadiene was 2.9 times more effective than piperylene as a fluorescence quencher. Examination of spectra failed to reveal any evidence of ground state complexing of reactants.

D. A triplet of 2-phenylthiophene (I) was then generated by sensitization (7). That a triplet can be formed is indicated by the fact that the photoreduction of benzophenone (excitation at 350 mμ, 0.1 M, E_T = 69 Kcal/mole) (8) with benzhydrol (0.1 M) to form benzpinacol in degassed benzene solution proceeds 22 times slower in the presence of I (5.3×10^{-3} M) than in its absence. Naphthalene, a known quencher of benzophenone triplets (9) at the same concentration produces a 14-fold rate retardation. Although promotion to the triplet appears to have been efficient, the 2-phenylthiophene was neither appreciably consumed nor was any detectable amount of rearrangement product II formed. Similarly acetophenone (E_T = 74 Kcal/mole) (8) failed to sensitize rearrangement.

We consider these data to be related to reported observations of singlet state quenching (10). The following general scheme, largely based on the pioneering work of Hammond (10a) is consistent with the results. Eqs. 1-5 apply at piperylene concentration of > 0.2 M where rearrangement does not account for more than 1.5% of the amount of I consumed (11).

$\underline{1} \xrightarrow{h\nu} \underline{1}^{*}_{1}$ (1)

$\underline{1}^{*}_{1} \xrightarrow{k_d} \underline{1}$ (2) Radiationless conversion; unknown but included for the sake of completeness

$\underline{1}^{*}_{1} \xrightarrow{k_f} \underline{1} + h\nu'$ (3)

$\underline{1}^{*}_{1} \xrightarrow{k_{isc}} \underline{1}^{*}_{3} \longrightarrow \underline{1}$ (4) isc = inter system crossing

$\underline{1}^{*}_{1} + P \xrightarrow{k_q} \text{products}$ (5) P = piperylene

The behavior of 2-phenylthiophene described in these experiments suggests to us that its valence bond rearrangement (1) proceeds at an excited singlet state level. The reaction of this state with dienes is a much more efficient process and takes precedence over rearrangement at moderate diene concentrations. In addition to providing a new probe into the mechanism of the valence bond isomerization this diene quenching suggests the possibility of photochemical Diels-Alder reactions for thiophenes.

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2. For recent photochemistry of other heteroaromatics see: (a) E.F. Ullman and B. Singh, ibid., **88**, 1844 (1966); (b) H. Tiefenthaler, W. Dörscheln, H. Göth and H. Schmid, Helv. Chim. Acta, **50**, 2244 (1967); (c) P. Beak, J.L. Miesel and W.R. Messer, Tetrahedron Letters, 5315 (1967); (d) B. Singh and E.F. Ullman, J. Am. Chem. Soc., **89**, 6911 (1967); (e) H. Hiraoka and R. Srinivasan, ibid., **90**, 2720 (1968); (f) E.E. van Tamelen and T.H. Whitesides, ibid., **90**, 3894 (1968).
3. Conc. I = 1.08×10^{-2} M; E_s = ca 95 Kcal/mole estimated from absorption and emission spectra (7b). Conc. piperylene = 1.03 M. No light is absorbed by piperylene in these experiments. Spectral overlap prevents carrying out a similar experiment with II.
4. Relative quantum yields for consumption of I were determined from plots of the rates of disappearance of I by glpc (6' DEGS, programmed 166-192°). Rate plots (8-12 points) were subjected to least square analysis by computer for which we thank Dr. Harriet Benson of our Department.
5. Associated Electrical Industries MS-9.
6. All attempts at isolation and purification of the photoproduct led to resinification. Desulfurization with Raney nickel of a fresh sample of photoproduct furnished several hydrocarbons (including 1-phenylbutane). The molecular weights of the new hydrocarbons are grouped at 196, 198, 200 and 202.

This corresponds to loss of sulfur from the photoproduct and addition of 0, 2, 4 and 6 molecules of hydrogen respectively. Neither singlet nor triplet products of piperylene are observable by glpc or mass spectrometry nor was piperylene appreciably consumed during photolysis. Structural investigations are obviously in progress.

7. (a) E_T = 53-60 Kcal/mole estimated from phosphorescence spectrum.
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11. Although traces (1-2%) of 3-phenylthiophene are formed, its accurate determination for rate purposes is not feasible.