

Short Communication

Quenching effect of five-membered ring heterocycles on the photoreduction and photocycloaddition reactions of benzophenone: II

R. A. BOLÍVAR, R. MACHADO, L. MONTERO, F. VARGAS and C. RIVAS

Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas 1010A (Venezuela)

(Received September 14, 1982)

1. Introduction

In contrast with furan and its methyl derivatives [1], which are excellent substrates for excited carbonyl compounds, heterocycles such as thiophene, pyrrole, selenophene, tellurophene and imidazole are either inert or poor substrates in oxetane-forming reactions.

Selenophene [2] requires at least one methyl group substituted in either the α or the β position to yield an oxetane in the presence of excited benzophenone and thiophene is capable of undergoing oxetane formation when at least two methyl groups are substituted in the ring [3]. However, for nitrogen heterocycles such as pyrrole [4] and imidazole [5] it is necessary to substitute an electron-attracting group on the nitrogen atom bearing the proton to make the ring susceptible to attack by excited carbonyl compounds such that it undergoes photocycloaddition reactions leading to a stable cyclic compound.

In this study we attempt to correlate inertness towards oxetane formation with the quenching activity of these heteroaromatic rings on the photoreduction reaction of benzophenone. As has been stated before [6] the reason for choosing the photoreduction of benzophenone to test for the quenching of oxetane formation is that it has been shown that the excited state of the aromatic ketones involved is the same for both types of reaction [7]. Thus the results obtained from these experiments can safely be applied to the photocycloaddition reaction.

In fact Stern-Volmer plots (Φ_0/Φ_Q versus $[Q]$) for thiophene and its monomethyl derivatives reported elsewhere [6] indicate that thiophene is a good quencher and furthermore that its monomethyl derivatives are even more efficient than the parent heterocycle.

The compounds studied in the present investigation were 2,5-dimethylthiophene, which was tested in order to complete the thiophene series, pyrrole, *N*-benzoylpyrrole, selenophene and imidazole.

2. Experimental details

Pyrrrole, imidazole and 2,5-dimethylthiophene (Aldrich) were purified before use. Selenophene [8] and *N*-benzoylpyrrole [9] were prepared by methods reported in the literature. Heterocycle concentrations ranging from 0 to 3.00 M were investigated. The concentrations required for complete inhibition [6] of the photoreduction reaction varied from one heterocycle to another (see the Stern–Volmer plots).

The reaction mixtures were irradiated using a carousel apparatus in a Rayonet reactor equipped with a set of low pressure mercury lamps ($\lambda = 350$ nm) with Pyrex filters. The disappearance of the n,π^* band of benzophenone at 335 nm was monitored using a Perkin–Elmer model 124 UV spectrometer.

3. Results and discussion

2,5-dimethylthiophene had a slight quenching effect and imidazole had no quenching effect whatsoever at concentrations ranging from 0 to 3 M. These results agree quite well with the fact that 2,5-dimethylthiophene undergoes a photocycloaddition reaction [3] and that imidazoles [10] yield substitution products, namely alcohols, which are presumably formed in a reaction sequence involving an unstable oxetane intermediate that is the precursor of the alcohol. However, when pyrrole was added to the benzophenone solution before irradiation the photoreduction was strongly quenched. This effect gradually increased as the concentration of pyrrole increased. The same effect was observed for selenophene. The form of the Stern–Volmer curve, which appears to be a segment of a parabola, is shown in Fig. 1. In contrast, *N*-benzoylpyrrole, which is a good substrate for excited carbonyl compounds, gives a curve of the same form but flattened at the bottom. For comparison the Stern–Volmer plots for the thiophene series are given in Fig. 2. Linear relations are obtained for these compounds.

The following Stern–Volmer equation holds for the mechanism suggested previously [6]:

$$\Phi_0/\Phi = 1 + K_q\tau[Q]$$

The mathematical equation for the curves shown in Figs. 1 and 3 for pyrroles and selenophenes respectively should be quadratic in $[Q]$ [11] as was verified by testing the data with a quadratic polynomial regression program [12]. This situation is commonly encountered when the quencher employed quenches two excited states [13]. However, for $K_q = 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$, which is a characteristic value, it has been reported [14] that a quencher concentration $[Q]$ of 1 M is required to quench a species with $\tau \approx 10^{-10} \text{ s}$ which may be the case for the S_1 state of benzophenone at room temperature. Since the curve shown in Fig. 1 was obtained for $[Q] = 10^{-2} \text{ M}$ it is very unlikely that pyrrole is an efficient quencher for the singlet state of benzophenone [15]. It would be more reasonable to assume that the only excited species in addition to the triplet state of benzophenone that can be quenched under these conditions is an exciplex formed between triplet excited benzophenone and a ground state molecule of pyrrole. Therefore the reaction scheme for the

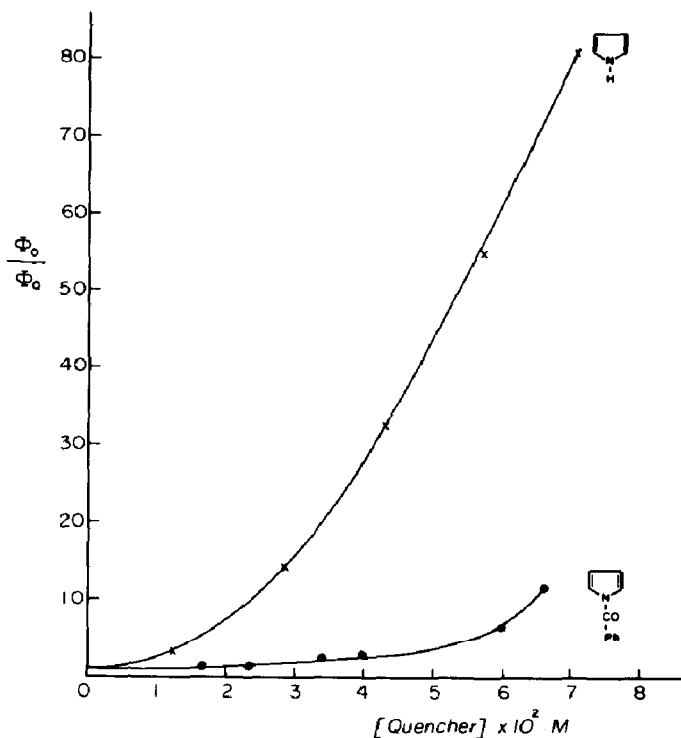


Fig. 1. Stern-Volmer plots for the quenching of benzophenone photoreduction by pyrrole and *N*-benzoylpyrrole.

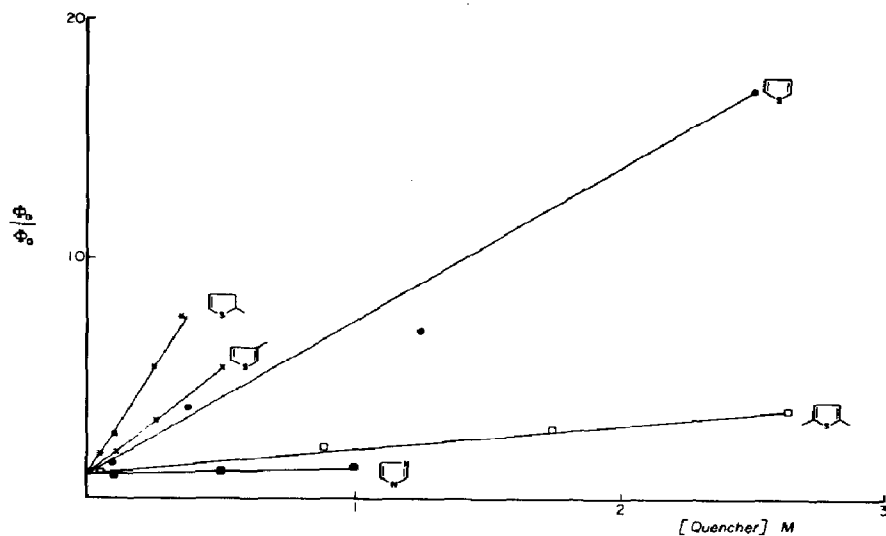


Fig. 2. Stern-Volmer plots for the quenching of benzophenone photoreduction by thiophene derivatives and imidazole.

photoreduction of benzophenone that would fit the experimental results using quenchers such as pyrrole and selenophene would be fundamentally the same as that reported for thiophene and its methyl derivatives [6] with the additional step

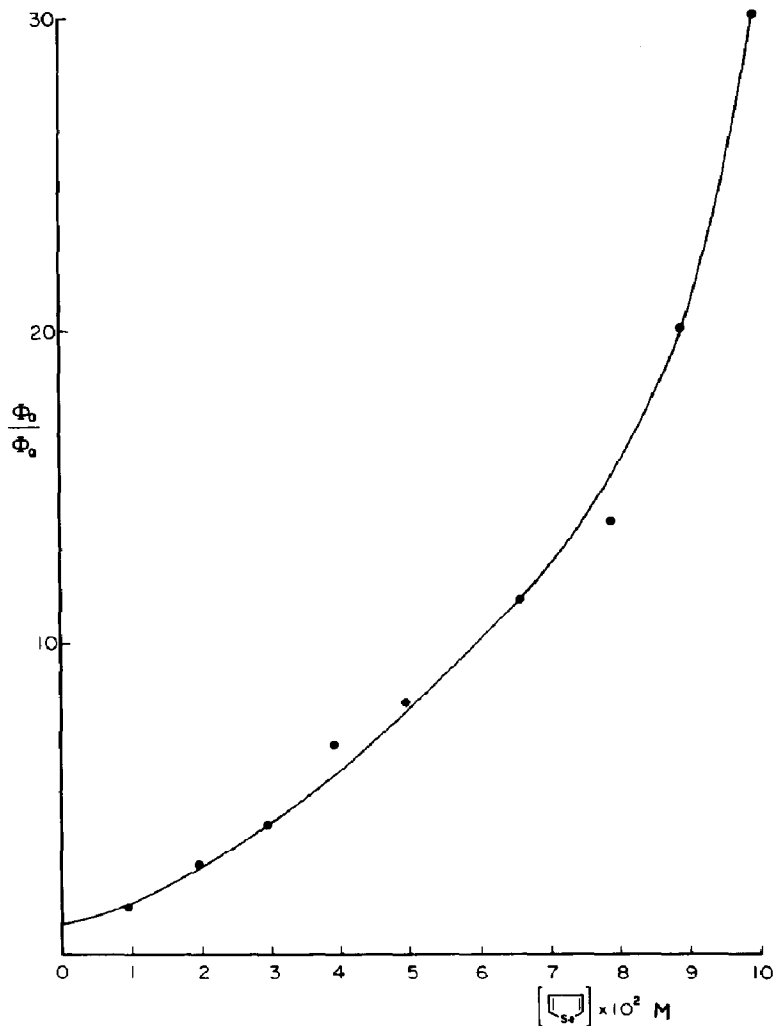
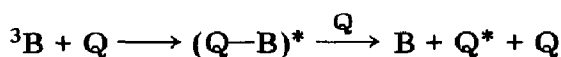


Fig. 3. Stern-Volmer plot for the quenching of benzophenone photoreduction by selenophene.



which would be essential to change the Stern-Volmer plot from a linear to a quadratic expression. Thus the following Stern-Volmer equation would hold for the proposed mechanism [13]:

$$\Phi_0/\Phi = (1 + K_q\tau[Q]) (1 + K_q'\tau'[Q]) \quad (1)$$

where Φ_0 and Φ are the quantum yields for the photoreduction of benzophenone in the absence and the presence of the quencher respectively. The mechanism for the quenching process of the exciplex discussed above should be subjected to further investigation before reaching any conclusion.

Other heterocycles such as 2- and 3-methylselenophene and tellurophene are in the process of being synthesized for quencher studies. The results will be used to approach synthetic work from a more systematic standpoint.

- 1 C. Rivas and E. Payo, *J. Org. Chem.*, **32** (1967) 2918.
- 2 C. Rivas, D. Pacheco and F. Vargas, *Actas Quim. Sudam.*, **2** (1982) 1.
- 3 C. Rivas and R. A. Bolívar, *J. Heterocycl. Chem.*, **10** (1973) 967.
- 4 C. Rivas and R. A. Bolívar, *J. Heterocycl. Chem.*, **13** (1976) 1037.
- 5 T. Nakano, C. Rivas, C. Pérez and J. M. Larrauri, *J. Heterocycl. Chem.*, **13** (1976) 173.
- 6 R. A. Bolívar and C. Rivas, *J. Photochem.*, **17** (1981) 91; **19** (1982) 95.
- 7 D. R. Arnold, *Adv. Photochem.*, **6** (1968) 301.
- 8 S. Gronowitz and T. Freid, *J. Heterocycl. Chem.*, **13** (1976) 1319.
- 9 A. Pietet, *Ber. Dtsch. Chem Ges.*, **37** (1904) 2797.
- 10 T. Matsuura, A. Banda and K. Ogura, *Tetrahedron*, **27** (1971) 1211.
- 11 C. Rivas, R. Machado, L. Montero and R. A. Bolívar, *9th IUPAC Symp. on Photochemistry, Pau, July 1982*.
- 12 *Hewlett-Packard 44E Owner's Handbook and Programming Guide*, Hewlett-Packard, 1980.
- 13 J. A. Barltrop and J. D. Coyle, *Excited States in Organic Chemistry*, Wiley, New York, 1975, p. 101.
- 14 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin, Menlo Park, CA, 1978, p. 261.
- 15 A. A. Lamola and N. J. Turro, *Energy Transfer and Organic Photochemistry*, Wiley-Interscience, New York, 1969, p. 83.