Tetrahedron Letters,Vol.25,No.28,pp 2931-2934,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

UNIMOLECULAR HETEROAROMATIC PHOTOINITIATORS[1]

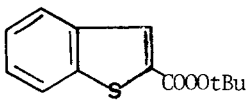
Douglas C. Neckers* and Frank L. Wagenaar
Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

Abstract: We report herein the synthesis and use for polymerization of new photoinitiators based on benzo(b)thiophene.

Several years ago we introduced the concept of phototunable free radical sources. The idea was to build a free radical source, such as a peroxide or a perester, into a molecule capable of absorbing light and, from the excited state so derived, convert the energy of the chromophore into a homolytic dissociation of the -O-O- bond.

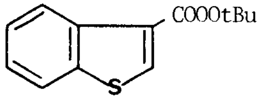
To this end we have published several studies which combine chromophoric systems the excited state characteristics of which are well known, with t-butyl perester functions. Properly designed these peresters combine facile photochemical reactivity with relative thermal stability. The first of these was based on benzophenone[2] and its photochemical and initiator characteristics are now well understood[3-5]. Later examples combined π,π^* excited states with the -O-O- t-butyl perester function.[6,7] Among the more interesting recent examples are of polymers based on p-(p'-vinyl)benzoyl tert-butyl perbenzoate. Some of these photoinitiators have the important characteristic of being water soluble.[5,8]

In this communication we report two new peresters I and II based on benzo(b)thiophene. Benzo(b)thiophene has an absorption spectrum similar to naphthalene[9] and like napthalene (Et 60 kcal/mole) is susceptible to energy transfer from typical triplet energy transfer donors.[10,11] Peresters I and II were easily prepared from the corresponding acid chlorides.[11] Both compounds were white crystalline solids and stable indefinitely in the cold.



I

m.p. = 50-2°
n.m.r. δ = 1.42(5,9H)
= 7.14-.84(m,4H)
= 8.00(5,1H)



II

m.p. = 49.5-50°
n.m.r. δ = 1.40(5,9H)
= 7.24-.86(m,3H)
= 8.36-.37(m,1H)

The decomposition of I and II occurs at a reasonable rate when they are irradiated at 300 nm, and I has a quantum yield of dissociation in benzene of 0.75. This is comparable to the quantum yield of dissociation of p-benzoyl tert-butyl perbenzoate at 366 nm (ϕ = .86)[1] under similar conditions. The photochemical dissociation of perester II is non-linear and faster than the dissociation of I. In both cases the products of decomposition interfere with continued decomposition, and after 10% or so reaction, the rates decrease.

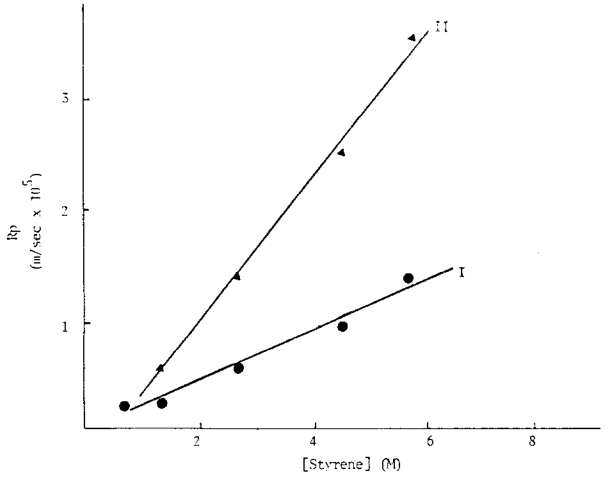
The rate of polymerization of MMA is a function of monomer concentration when I and II are irradiated under standard conditions.[2-4] In bulk monomer when irradiated at 300 nm, I gave an initial rate of 4.83 x 10^{-4} m/sec and II 5.63 x 10^{-4} m/sec. After 30 minutes ($[\mathrm{Init.}]_o$ = 2.4 x 10^{-3} m), the % conversion vs. time plots became nonlinear for both initiators. When irradiated at 366 nm there is no polymerization with either perester but in the presence of benzophenone, a known triplet energy transfer donor, the rate of polymerization of MMA initiated by I is obviously increased. Thus under conditions where no benzo(b)thiophene absorption is occurring, perester I can be forced to initiate polymerization at a rate similar to direct irradiation polymerization at 300 nm. This is in distinct contrast to the case with benzoyl peroxide[1].

Styrene quenches n,π^* triplets.[2-7] thus its polymerization is a particularly good test of the effectiveness of a specific photoinitiator for aromatic monomers. If the rate of polymerization increases with styrene concentration, there is no quenching. On the other hand, a decrease with styrene concentration indicates that the monomer is quenching the excited state of the initiator.[2-7]

As is shown in Figure 1, neither I nor II is quenched by styrene monomer. In both cases the rate of polymerization increases as a function of monomer concentration. As can be shown in other related systems[12,13] the rate of formation of radicals from 3-benzo(b)-thiophene dissociable functions is somewhat faster than from the corresponding 2-benzo(b)-thiophene analogs. This is particularly apparent in the rates of polymerization of styrene as initiated by the benzo(b)thiophene isomeric peresters, I and II.

Figure 1

R_p vs [Styrene].



We have also studied another photoinitiator based on benzo(b)thiophene, 2,3-dibromobenzo-(b)thiophene. This initiator decomposes by homolysis of the 3-carbon-bromine bond (reference 1) and it is most effective. The effectiveness of 2,3-dibromobenzo(b)thiophene is compared to I and II for MMA in Figure 2.

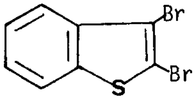
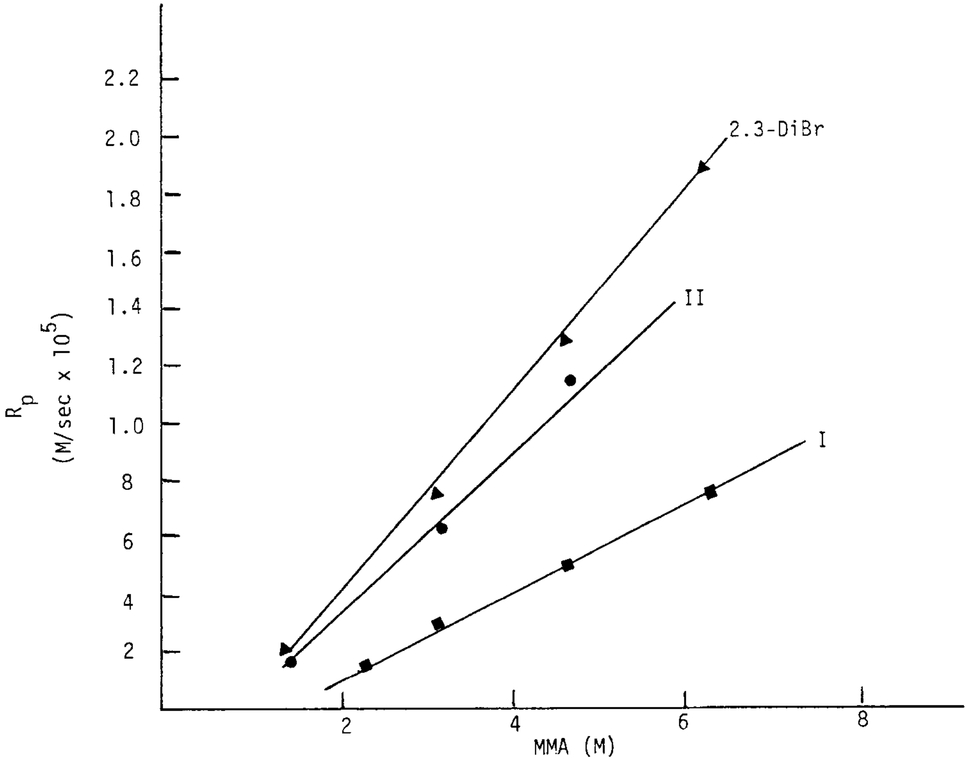


Figure 2

R_p vs. [MMA]



Finally, both perester systems compare in photoinitiation efficiency with the commercial photoinitiators diethoxyacetophenone and 1-phenyl-1,2propanedione oxime though the commercial initiators retain their effectiveness at longer wavelengths (366 nm) while I and II do not.[14]

References

1. Taken, in part, from the M.S. thesis of F. L. Wagenaar, Bowling Green State University, August 1983.

2. L. Thijs, S. N. Gupta, and D. C. Neckers. J. Org. Chem., 44, 4123 (1979).

3. S. N. Gupta, I. Gupta, and D. C. Neckers. J. Polym. Sci. Polym. Chem. Ed., 19, 103 (1981).

4. S. N. Gupta, L. Thijs, and D. C. Neckers. J. Polym. Sci. Polym. Chem. Ed., 19, 855 (1981).

5. I. Gupta, S. N. Gupta, and D. C. Neckers. J. Polym. Sci. Polym. Chem. Ed., 20, 147 (1982).

6. I. I. Abu-Abdoun, L. Thijs, and D. C. Neckers. J. Polym. Sci., Poly. Chem. Ed., 21, 3129 (1983).

7. I. I. Abu-Abdoun, L. Thijs, and D. C. Neckers. Macromolecules, in press, March 1984.

8. I. Gupta and D. C. Neckers, unpublished.

9. A. H. A. Tinnemans and D. C. Neckers, "The Photochemistry of Benzo(b)furan, Benzo(b)thiophene and Indole; W. Horspool, Ed., Wiley-Interscience, in press.

10. J. Dopper and D. C. Neckers, J. Org. Chem., 35, 1582 (1970).

11. A. H. A. Tinnemans and D. C. Neckers, J. Org. Chem., 43, 2493 (1978).

12. F. L. Wagenaar and D. C. Neckers, J. Org. Chem, 46, 3939 (1981).

13. F. L. Wagenaar and D. C. Neckers, J. Org. Chem., to be published.

14. This work has been supported by N.S.F. (DMR #8103100). The authors are grateful for this support. The authors also acknowledge many helpful discussions with Professor Satyendra Gupta.

(Received in USA 19 March 1984)