Photoadditions of an Alicyclic Thioketone

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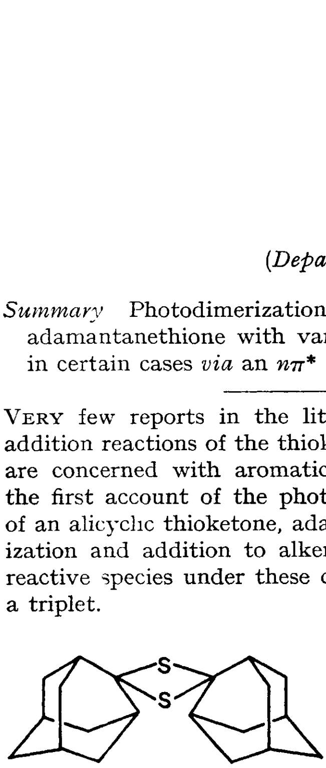
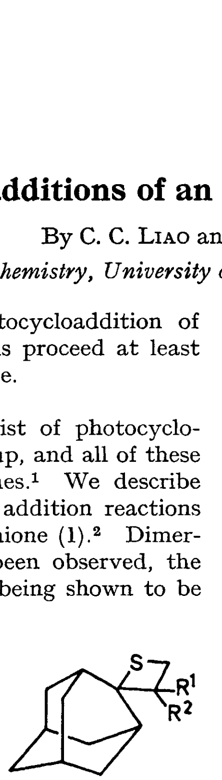
Summary Photodimerization and photocycloaddition of adamantanethione with various olefins proceed at least in certain cases *via* an $n\pi^*$ triplet state.

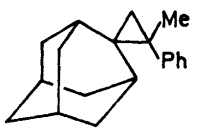
Very few reports in the literature exist of photocycloaddition reactions of the thioketone group, and all of these are concerned with aromatic thioketones.[1] We describe the first account of the photochemical addition reactions of an alicyclic thioketone, adamantanethione (1).[2] Dimerization and addition to alkenes have been observed, the reactive species under these conditions being shown to be a triplet.



(2)

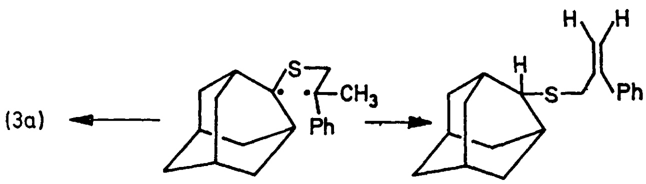


(3)



(5)

a; R^1 = CH_3, R^2 = Ph
b; R^1 = CD_3, R^2 = Ph
c; R^1 = H, R^2 = OEt
d; R^1 = R^2 = Ph



(7) (4)

Irradiation of (1) in n-pentane (254 nm) gave the dimer (2).† The same product was obtained in benzene solution with light of longer wavelength (>420 nm) (in a very much slower reaction‡) or when sensitized with benzophenone.

The reaction at longer wavelength‡ appears to proceed through the lowest (n,π^*)[4] triplet (E_T 52·5 kcal/mole), but more complete information concerning this species was obtained by a study of its addition to alkenes.

Irradiation ($\lambda > 420$ nm) of adamantanethione and α-methylstyrene in benzene gave the thietan (3a): n.m.r. (CCl_4) δ 1·93 (3H, s), 2·50 (1H, d, *J* 10Hz), and 3·70 (1H, d, *J* 10Hz); m^+/e 284 and 238; and 2-adamantyl 2′-phenylallyl sulphide (4): n.m.r. (CCl_4) δ 3·0 (1H, broad), 3·5 (2H, s), 5·2 (1H, d, *J* 2Hz), and 5·4 (1H, d, *J* 2Hz); m^+/e 284, 149, and 135. The structure of (4) was established by independent synthesis from adamantane-2-thiol and 2-phenylallyl bromide. The structure of (3a), which followed from the mass spectrum, was substantiated by Raney nickel reduction[5] to the spiroadamantane (5): n.m.r. (CCl_4) δ 0·38 (1H, d, *J* 5Hz), 1·02 (1H, d, *J* 5Hz), 1·44 (3H, s), m^+/e 252; and 2-methyl-2-(1′-phenylvinyl)adamantane (6): n.m.r. (CCl_4) δ 1·53 (3H, s), 4·78 (1H, m), and 5·00 (1H, broad); m^+/e 252, 237, and 149. The formation of products from irradiation of adamantanethione and α-methylstyrene could be rationalized by the mechanism now well established for oxetan formation *via* a triplet.[6] An intermediate thiatetramethylene (7) could give (3a) by cyclisation or (4) by hydrogen abstraction. This has been unequivocally substantiated by irradiation of adamantanethione and α-trideuteriomethylstyrene to give trideuteriated (3b) and deuteriated (4) [>CD·S·CH_2(Ph)·C:CD_2). When a mixture of deuteriated and undeuteriated α-methylstyrene was used, compound (4) contained either three deuterium atoms or none. No intermolecular transfer of hydrogen (deuterium) was observed. The isotope effect of the intramolecular hydrogen abstraction was found to be 2·0.

Similar thietans§ (3c) and (3d) were isolated when ethyl vinyl ether and 1,1-diphenylethylene were used as substrates. In the cases of *trans*-stilbene and fumaronitrile, adducts were also obtained but two stereoisomeric thietans§ were formed and in both cases the starting olefins were found to be isomerized at the conclusion of the experiment.

The addition to ethyl vinyl ether was investigated in more

† J. W. Griedanus has obtained (2) in a ground-state reaction. We have demonstrated the structure of the dimer (*M* 358, osmometer) m^+/e 322, n.m.r., ($CDCl_3$): δ 1·43—2·06 (24H, m) and 2·38 (4H, broad singlet) by chemical conversion (Raney nickel) into adamantane; Berchtold[3] has reported the formation of cyclohexanethione dimer by irradiating cyclohexanone ethylenedithioacetal.

‡ The reaction at shorter wavelength may well be from a different excited state: the matter is being studied.

§ Satisfactory analysis and spectroscopic data were obtained.

detail. At a concentration of 0·2M-adamantanethione in benzene containing 2M-ethyl vinyl ether the quantum yield for adduct formation (*ca.* $4{\cdot}6 \times 10^{-4}$) was very low. The reaction was, nonetheless, clean and gave a high chemical yield (*ca.* 75%) of product. The reaction could be sensitised with Michler's ketone, benzophenone, and triphenylene. It was found that the efficiency of the reaction was identical (±10%) whether the energy was introduced into the molecule directly or *via* a sensitiser (Michler's ketone), which, in view of the efficient intersystem crossing of the ketone, indicated an equivalent efficiency in intersystem crossing for the thioketone, *i.e.* near unity. The reaction could be quenched by both 9-methylanthracene and cyclooctatetraene giving Stern–Volmer slopes of $9{\cdot}14\text{M}^{-1}$ and $2{\cdot}17\text{M}^{-1}$, respectively. A linear plot was obtained from a dilution curve (varying the concentration of olefin) and the bimolecular rate constant of thiatetramethylene (or complex) was calculated, with the usual steady state assumptions, to be $4{\cdot}4 \times 10^{7}\text{M}^{-1}\,\text{s}^{-1}$.

Further it was evident that an energy-wasting reversible process, as in enone addition[7] or oxetan formation,[8] also occurred in thietan formation. The partition function between the thiatetramethylene (or complex) going on to product or reversing to starting material[7] was found to be 1:350.

It was also found that the quantum yield of adduct was also dependent on thioketone concentration, decreasing with higher concentrations, and a linear plot was obtained of reciprocal of quantum yield against concentration of adamantanethione (slope: $9{\cdot}35 \times 10^{3}\text{M}^{-1}$). Evidently, here self-quenching, perhaps of the type described by Chapman[9] for aromatic π,π^* triplet states is operative, although the species here involved is of n,π^* character. From the relation of quantum yield to thioketone concentration the self-quenching rate constant can be extracted and is of the order of $10^{9}\text{M}^{-1}\,\text{s}^{-1}$. Since the amount of dimer formation is minuscule, this implies that the partition function in dimerisation enormously favours reversal by several orders of magnitude. This is, of course, in agreement with the extremely slow rate of dimer production on long-wavelength irradiation. The nature of this process is under investigation.

(*Received, September 17th*, 1971; *Com.* 1628.)

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