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PHOTOCYCLOADDITION OF THIOCARBONYL COMPOUNDS TO OLEFINS. THE REACTIONS OF THIOBENZOPHENONE WITH CASE-III OLEFINS.

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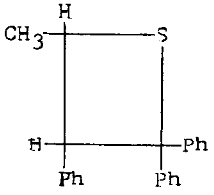
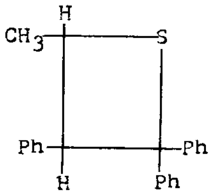
In our previous papers, it has been reported that the photocycloaddition of n,π^* triplet state of thiobenzophenone to olefins substituted by electron-releasing groups (case-I olefins) affords 1,4-dithianes(1,2), while the reaction of π,π^* state of thiobenzophenone results in the formation of thietanes with olefins activated by electron-withdrawing groups (case-II olefins)(3).

In this paper, we would like to report the third group of olefins (case-III olefins) in the photocycloaddition of thiobenzophenone: namely, olefins bearing electron-releasing substituents afford thietane derivatives by the irradiation with 5890Å light from a sodium lamp. When a mixture of thiobenzophenone and *trans*-propenylbenzene was irradiated with 5890Å light for 20hr in an atmosphere of carbon dioxide, crystals of *trans*-2,2,3-triphenyl-4-methylthietane, I, was obtained in 63% yield after excess olefin had been removed: mp 78 - 9° (*Anal.* Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37. Found: C, 83.84; H, 6.73.); nmr signals (δ, $CDCl_3$) 7.40 - 6.96 m (13H), 6.90 - 6.70 m (2H), 4.86 d (1H), 3.97 dq (1H), and 1.38 d (3H). On the other hand, the reaction with *cis*-propenylbenzene under the same condition gave a mixture of I (79%) and II (21%) in 63% overall-yield(4). In this case, the recovered olefin was analyzed by vpc and was found to be a mixture of *cis*- and *trans*-isomers with the ratio of 41:59. Similarly,

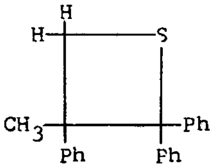


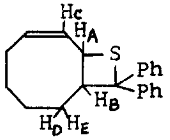
I



II

2,2,3-triphenyl-3-methylthietane, III, was obtained in 90% yield by the reaction with α-methylstyrene: mp 112 - 3° (Anal. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37. Found: C, 83.72, H, 6.38.); nmr signals (δ, $CDCl_3$) 7.60 - 6.90 m (15H), 4.05 d (1H), 2.92 d (1H), and 1.68 s (3H). The photocycloaddition of thiobenzophenone

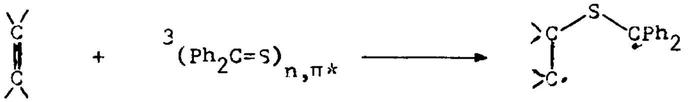

III


IV

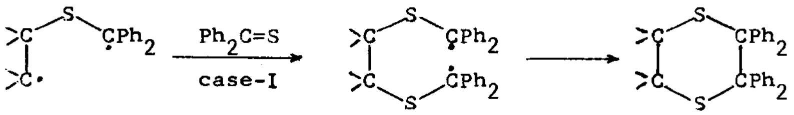
to 1,3-cyclooctadiene has been reported to give a thietane derivative, IV, by the irradiation with ultraviolet light(5). We have found that the same reaction also takes place by the irradiation with 5890Å light.

We believe that the thietanes arise from n,π* triplet state of thiobenzophenone on the following evidence: (i) The light employed for the irradiation (5890Å) excites only n,π* transition of thiobenzophenone(6). (ii) The orientation of the addition of thiobenzophenone is predicted from considerations of the most stable diradical intermediate and/or of electrophilic attack of a sulfur atom in thiobenzophenone, analogous to the photocycloaddition of benzophenone(7). (iii) The isomerization of the olefin takes place during the reaction(8).

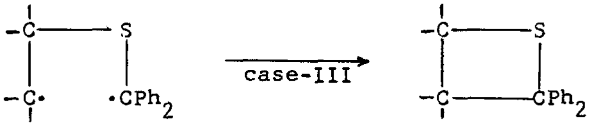
We have proposed that the photocycloaddition of thiobenzophenone to case-I olefins proceeds through the addition of n,π* triplet state of thiobenzophenone (1,2):


V

If the reaction of the composite radical V with another molecule of thiobenzophenone is faster than the recombination of the radical centers (case-I olefins), it gives 1,4-dithianes as the final product by the following sequence:



The reaction with case-III olefins, on the other hand, results in the formation of thietane derivatives by simple recombination of radical centers:



In the light of our observations that cyclohexene and styrene belong to case-I but 1,3-cyclooctadiene, propenylbenzene, and α-methylstyrene are case-III olefins, the key-factor to differentiate these two groups of olefins seems to be the steric inhibition by substituent(s) in case-III olefins to the reaction of V with another molecule of thiobenzophenone. From the viewpoint of stabilization effect of substituent(s) on the radical center, no distinct reduction of reactivity of V toward thiobenzophenone can be expected for case-III olefins.

References

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2. A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, J. Amer. Chem. Soc., in press.
3. A. Ohno, Y. Ohnishi, and G. Tsuchihashi, Tetrahedron Lett., in press.
4. Although II could not be isolated in pure state, the structure was confirmed by nmr. Satisfactory elemental analyses have been obtained for a mixture of I and II and the composition of a mixture has been determined by nmr.
5. K. Yamada, M. Yoshioka, and N. Sugiyama, J. Org. Chem., 33, 1240 (1968). We have confirmed the structure by nmr study: the spin-coupling constants were determined as J_{AB}= 10.0Hz, J_{BD}= 10.0Hz, J_{AC}= 5.0Hz, and J_{BE}= 3.4Hz by spin-decoupling technique. See also Y. Omote, M. Yoshida, K. Yoshioka, and N. Sugiyama, ibid., 32, 3676 (1967) for the reaction with cyclohexadiene.
6. O. Korver, J. U. Veenland, and Th. J. de Boer, Rec. Trav. Chim. Pays-Bas, 84, 289 (1965).

7. N. J. Turro, "*Molecular Photochemistry*," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 208 - 11.

8. We have found that the equilibrium composition of propenylbenzene (*cis*/*trans* = 2/98 at 27°) is quite different from that expected from the thermodynamical stabilities of these isomers (*cis*/*trans* = 22/78 at 27°)(9). The detail discussion on this subject will be published elswhere.

9. J. A. Kilpatrik, C. W. Beckett, E. J. Prosson, K. S. Pitzer, and F. D. Rossini, *J. Res. Natl. Bur. Stand.*, **42**, 225 (1949).