Tetrahedron Letters No.3, pp. 161-164, 1969. Pergamon Press. Printed in Great Britain.

PHOTOCYCLOADDITION OF THIOCARBONYL COMPOUNDS TO OLEFINS. THE REACTIONS OF THIOBENZOPHENONE WITH ELECTRON-DEFICIENT OLEFINS.

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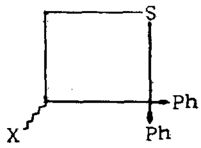
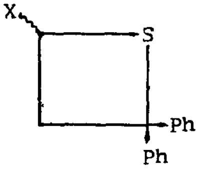
(Received in Japan 16 November 1968; received in UK for publication 8 December 1968)

It has been reported that the photocycloaddition of thiobenzophenone to olefins substituted by electron-releasing groups (case-I olefins) affords 1,4-dithianes(1). The reaction has been found to be quite stereospecific and to take place by the irradiation with either 3660Å light from a high-pressure mercury lamp or 5890Å light from a sodium lamp.

In the present study, we have found that the photocycloaddition of thiobenzophenone with olefins activated by electron-withdrawing groups (case-II olefins) results in the formation of thietane derivatives. When a mixture of acrylonitrile and thiobenzophenone was irradiated by 3660Å light for four days in a carbon dioxide atmosphere, crystals of 3-cyano-2,2-diphenylthietane, Ia, were obtained in 93% yield after excess acrylonitrile had been removed: mp 83.5 - 4.5° (*Anal*. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57; S, 12.75. Found: C, 76.67; H, 5.21; N, 5.73; S, 12.73.); ν^{KBr} 2250 cm^{-1} (C≡N); nmr signals (δ, $CDCl_3$) 7.70 - 7.09 m (10H), 4.93 t (1H), 3.50 t (1H), and 3.23 t (1H). The mass spectrum was indicative of the position of the cyano group. Peaks were found at *m/e* 251 (M^+), 224 (M^+- HCN), 205 (NC-CH=C(Ph)$_2$), 45 (CH≡S^+), and 198, 165, 121, 91, 77, and 51 (fragments of thiobenzophenone). When Ia was



I



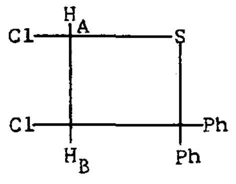
II

a: X = CN
b: X = CH_3OCO
c: X = CH_3COO

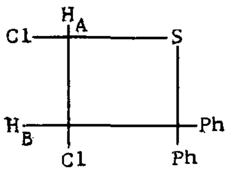
oxidized to the corresponding sulfone (mp 157 - 8.5°) by hydrogen peroxide, three triplets in the nmr spectrum of Ia appear at 4.50 - 4.14 as an ABC multiplet. Thus, the structure of the product has been unambiguously determined to be Ia and no indication for the contamination of IIa was noticed. It is worth noting that the direction of addition of thiocarbonyl compound to acrylonitrile is reverse to that of carbonyl compound; as recently reported, acetone adds with acrylonitrile to afford 4-cyano-2,2-dimethyloxetane rather than its 3-cyano-isomer(2).

Irradiation of thiobenzophenone in the presence of methyl acrylate or vinyl acetate gives 3-methoxycarbonyl-2,2-diphenylthietane, Ib (mp 84 - 5°)(3), in 81% yield or 3-acetoxy-2,2-diphenylthietane, Ic (mp 114.5 - 5.5°)(3), in 30% yield,respectively.

The highly stereospecific character of the reaction was established by the reaction with <u>cis</u>- and <u>trans</u>-dichloroethylenes. The reaction with <u>cis</u>-dichloroethylene exclusively afforded <u>cis</u>-3,4-dichloro-2,2-diphenylthietane, III, in 83% yield: mp 126 - 7° (<u>Anal</u>. Calcd for $C_{15}H_{12}Cl_2S$: C, 61.02; H, 4.10; Cl, 24.02; S, 10.86. Found: C, 61.29; H, 4.07; Cl, 24.16; S, 10.77.); nmr signals (δ, $CDCl_3$) 7.73 - 7.06 m (10H), 6.17 d (1H), and 5.66 d (1H) with J_{AB}= 6.7Hz. On the other hand, the reaction with <u>trans</u>-dichloroethylene resulted in the formation of the <u>trans</u>-isomer, IV, in 90% yield: mp 72 - 3° (<u>Anal</u>. Calcd for $C_{15}H_{12}Cl_2S$: C, 61.02; H, 4.10; Cl, 24.02; S, 10.86. Found: C, 60.96; H, 4.04; Cl, 23.91; S, 10.86.); nmr signals (δ, $CDCl_3$) 7.58 - 7.05 m (10H), 5.75 d (1H), and 5.36 d (1H) with J_{AB}= 7.8Hz. The configurations of the two isomers were unequivocally determined by the measurement of dipole moments: 2.16D for III and 2.02D for IV. Further, <u>trans</u>-3,4-dicyano-2,2-diphenylthietane (mp 144 - 4.5°)(3) was obtained from fumaronitrile by the same reaction.



III

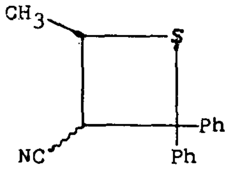


IV

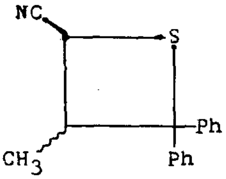
In contrast to case-I olefins, the reaction with case-II olefins did not proceed by the irradiation with 5890Å light from a sodium lamp. Since the irradiation was conducted in a Pyrex apparatus, the species first excited should be thiobenzophenone; these case-II olefins are transparent under this condition. Furthermore, since no essential difference was observed in uv spectrum of thiobenzophenone in acrylonitrile (λ_{max}= 321 mμ) from that in ethanol(4), the absorption takes place through a π,π^* band of thiobenzophenone but not through a charge-transfer band of thiobenzophenone to an olefin. Evidently, the π,π^* state of thiobenzophenone plays a role in the reaction. By considering the highly stereospecific nature of the cycloaddition, the mechanism of the reaction may be most plausively explained in terms of an electron transfer from the π^* orbital of the π,π^* state of thiobenzophenone to anti-bonding orbital of electron-deficient double bond of case-II olefin(5). This mechanism is also supported by the fact that the yields of the adducts, Ia, Ib, and Ic,are in the order of electron-deficiency in double bond of the starting olefins:

$$-CN > -COOCH_3 > -OCOCH_3$$

In this connection, it is quite interesting that the reactions with both *cis*- and *trans*-crotononitrile result in the formation of 2:1 mixture of V and VI in almost quantitative yields. In these reactions, again configurations of



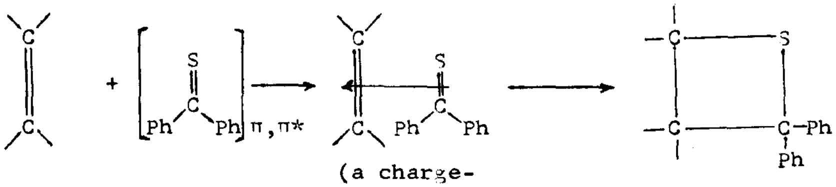
V



VI

starting olefins are retained in the products; the *cis*-olefin to the *cis*-thietane and the *trans*-olefin to the *trans*-thietane. Conceivably, electron deficiency at β-carbon in these olefins is somewhat weakened by electon-releasing ability of methyl group and, as a result, the orientational specificity observed in the reaction with acrylonitrile no longer holds in that with crotononitrile.

Accordingly, the mechanism of the reaction with case-II olefins can be depicted as



(a charge-transfer complex)

Acknowledgement. The authors are greateful to Prof. T. Shimozawa of the Saitama University for his measurement of and useful discussions on dipole moments.

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3. Satisfactory elemental analyses have been obtained for these compounds. The structures have been confirmed by nmr, ir, and mass spectra, as done for Ia.
4. The λ_{max} for the transition of ground-state thiobenzophenone to the π,π^* state is 316.5 mμ, while that to n,π^* state is 599 mμ in ethanol. There is another absorption band at λ_{max}= 235 mμ: (a) H. C. Heller, *J. Amer. Chem. Soc.*, **89**, 4288 (1967); (b) O. Korver, J. U. Veenland, and Th. J. de Boer, *Rec. Trav. Chim. Pays-Bas*, **84**, 289 (1965).
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