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PHOTOCYCLOADDITION OF THIOCARBONYL COMPOUNDS TO MULTIPLE BONDS.

XI. PHOTOADDITION OF DI-*t*-BUTYL THIOKETONE WITH OLEFINS[1]

Atsuyoshi Ohno, Misao Uohama, Kaoru Nakamura, and Shinzaburo Oka
Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, JAPAN

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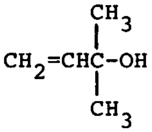
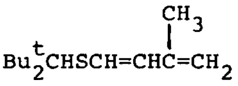
Within a recent decade, considerable progress has been made in the photochemistry of thiones.[2] Most studies, however, have been focused on the photochemistry of aromatic thiones and only a few reports describe the photochemistry of aliphatic thiones. Namely, alicyclic thiones undergo photocycloadditions in the presence of olefins.[3] Only one exception can be seen in the reaction of adamantanethione with α-methylstyrene, where an open-chain photo-adduct was isolated in addition to a cycloadduct.[3a] We now wish to report the result from photo-addition of di-*t*-butyl thioketone (1)[4] with various olefins, where no cycloadduct was obtained.

As a standard procedure, a mixture of 500 mg of 1 and 5 ml of an olefin was sealded in a Pyrex tube (10 mmϕ) under an atmosphere of nitrogen and was subjected to the irradiation with light from a 500 W high-pressure mercury lamp at a temperature of running water. After the color of the mixture disappeared, the olefin was removed under a reduced pressure and the residue was chromatographed on a column of silica gel with an appropriate eluent (benzene, hexane, or their mixture). Analytically pure products were obtained after preparative vapor-phase chromatography (1% Dexil). It was confirmed that oleifns employed for the reaction do not absorb the light of wavelength longer than 300 nm. Products and their yields are summarized in Table 1. Structures of products[5] were elucidated from nmr, ir, and mass spectral data and, in part, by comparing their physical properties with those of the corresponding authentic samples. Structures of the photo-adducts from 1-hexene were further confirmed by oxidiz-

Table 1. Photo-reaction of Di-*t*-butyl Thioketone with Olefins

Olefin	Reaction Time, hr	Yield of Products, %[a]			
		Bu^t_2CHSH	$(Bu^t_2CHS)_2$	Others	
$CH_2{=}CHC_4H_9$	72	—[b]	—[b]	$Bu^t_2CHSCH{=}CHCH_2C_3H_7$ $Bu^t_2CHSCH_2CH{=}CHC_3H_7$	92[c]
$CH_2{=}CHCH_2OH$	36	18	8	$Bu^t_2CHSCH_2CH_2CHO$ $Bu^t_2CHSCH_2CH{=}CH_2$	31 18
 $CH_2{=}CH\underset{CH_3}{\overset{CH_3}{C}}{-}OH$	12	30	—[b]	 $Bu^t_2CHSCH{=}CH\overset{CH_3}{C}{=}CH_2$	54
$CH_2{=}CHOCOCH_3$	6 weeks	3	—[b]	$Bu^t_2CHSCH{=}CHOCOCH_3$	41
$CH_2{=}CHOC_2H_5$	18	17	7	$Bu^t_2CHSCOCH_3$	47

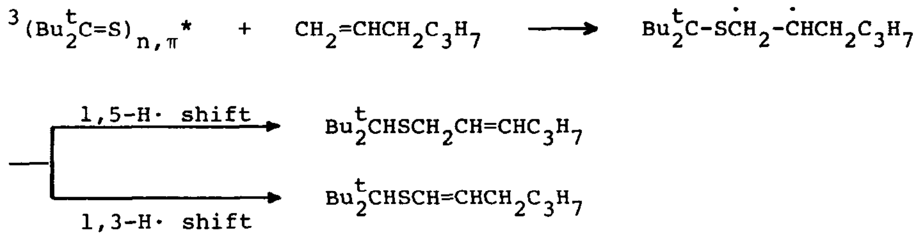
[a] Based on the consumed thioketone. [b] Not detected. [c] Yield of the mixture.

ing them to the corresponding sulfones.

Although there is no definite evidence, we assume that n,π^* triplet state of 1 (E_T = 43 ~ 45 kcal/mole)[6] is responsible to the reaction, because (a) electron-deficient olefins such as methyl acrylate and acrylonitrile do not react with 1,[7,8] (b) polymerization of styrene takes place in the presence of 1, (c) higher concentrations of 1 retard the reaction,[2b,3a,9] and (d) the reaction sequence more or less resembles to those of other thiones in their n,π^* triplet states.[2] That is, all reaction products are ascribable to the formation of 1,4-biradical intermediates followed by a 1,5- or 1,3-hydrogen migration; as a typical example, the reaction with 1-hexene may undergo as followings:

$$Bu^t_2C{=}S \xrightarrow{>300\text{ nm}} {}^1(Bu^t_2C{=}S)_{\pi,\pi^*}$$

$${}^1(Bu^t_2C{=}S)_{\pi,\pi^*} \longrightarrow {}^3(Bu^t_2C{=}S)_{n,\pi^*}$$



$$^{3}(\mathrm{Bu^{t}_{2}C{=}S})_{n,\pi}{}^{*} + \mathrm{CH_2{=}CHCH_2C_3H_7} \longrightarrow \mathrm{Bu^{t}_{2}\dot{C}{-}SCH_2{-}\dot{C}HCH_2C_3H_7}$$

$$\xrightarrow{1,5\text{-H}\cdot\ \text{shift}} \mathrm{Bu^{t}_{2}CHSCH_2CH{=}CHC_3H_7}$$

$$\xrightarrow[1,3\text{-H}\cdot\ \text{shift}]{} \mathrm{Bu^{t}_{2}CHSCH{=}CHCH_2C_3H_7}$$

Steric effect of two *t*-butyl groups seems to prevent the biradical intermediate from cyclization to a thietane.

It is interesting to point out that the present reaction proceeds with regiospecificity. However, the specificity is different from those of thiobenzophenone[8b] and adamantanethione.[2b] The photo-excited 1 prefers to attack relatively unactivated carbon atom. This is illustrated by the facts that 1 not only fails to react with electron-deficient olefins but also avoids attacking the terminal methylene group of ethyl vinyl ether, an electron-rich olefin, and that it reacts, though very slowly, with vinyl acetate, which is the weakest case-II olefin so far studied and do not react with thiobenzophenone of the n,π^* triplet state.[2a] Detailed studies on the mechanism of the reaction is in progress in our laboratory.

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