NOTES

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Photochemical Reduction of Di-*t*-butyl Thioketone

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Synopsis. Photochemical reduction of the title compound has been studied and the result is compared with that from the reaction with thiobenzophenone, an aromatic thioketone.

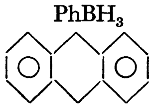
In a previous communication, we reported the result from the photoreaction of di-*t*-butyl thioketone (**1**) in the n,π^* triplet state (T_1, E_T=43—45 kcal/mol) with various olefins.[1)] The thioketone **1** reacted with electron-rich olefins affording open-chain photoadducts instead of cycloadducts. This is a marked contrast between **1** and other thioketones such as thiobenzophenone and adamantanethione.[2)]

It is known that thiobenzophenone in the n,π^* triplet state abstracts a hydrogen from various hydrogen-donors yielding the corresponding thiol or disulfide.[2,3)] Hydrogen-abstraction by aliphatic thioketones are scarcely studied,[2,4)] and we now wish to report some interesting observation in the photohydrogen-abstraction of **1** from various hydrogen-donors.

Results and Discussion

The photo-irradiation was continued until the color of **1**(λ_{max}=540 nm) disappeared. The reaction is summarized in Table 1. Since hydrogen-donors presently employed for the reaction have no absorption above 300 nm, there is no doubt that the reaction takes place through the excitation of **1** into the n,π^* singlet state (S_1) with the lights of 550 and 580 nm.[5)] Namely, it has been confirmed that the reaction of tetraphenylethylene with thiobenzophenone under the irradiation for 60 days with the light of 589 nm from sodium lamps (8×60 W)[6)] yields 9,10-diphenylphenanthrene. The photoreaction of 9,10-dihydroanthracene with thiobenzophenone has already been reported.[7)] Although we did not study the reaction quantitatively, existence of self-quenching, that is, the retardation of reaction by the increase of the concentration of **1**, suggests that the T_1 state of **1** is responsible to the reaction.[2,8)]

TABLE 1. PHOTOREDUCTION OF DI-*t*-BUTYL THIOKETONE

Hydrogen-donor	Reaction time, day	Yield of Bu$^t_2$CHSH, %
PhBH$_3$	28	72
 /in C_6H_6 (400 mg) (10 ml)	21	85[a)]
Ph_2C=CPh_2/in C_6H_6 or $CHCl_3$ (800 mg) (10 ml)	14	70[b)]
PhCH$_2$OH	6	82[c)]
EtOH	≈60	0[d)]
i-PrOH	≈60	0[d)]
Et$_3$N	2	80
i-BuNH$_2$	7	27[e)]
PhNH$_2$/in EtOH (5 ml) (10 ml)	28	24[f)]
Et$_2$O	≈60	0[d)]
	≈60	0[d)]

a) Anthracene was isolated in 90% yield. b) 9,10-Diphenylphenanthrene was isolated in 70% yield. c) Benzaldehyde was detected on VPC. d) No reaction took place. **1** was recovered quantitatively. e) **1** was recovered in 49% yield. f) **1** was recovered in 61% yield.

Table 1 reveals a remarkable reactivity of excited (S_1 or T_1) **1** toward the hydrogen-abstraction; generally, the reactivity of 2-propanol is larger than, or at least comparable to, that of toluene toward hydrogen-abstraction,[9,10)] whereas toluene and even tetraphenylethylene are much better hydrogen-donors than aliphatic alcohols and ethers in the present photo-reduction. The large reactivity of aromatic compound can be corelated with their ionization potentials[11)] and seems to imply the formation of a charge-transfer-type complex between **1** (in S_1 or T_1) and a hydrogen-donor. Similar process has been suggested for the photoreductions of benzophenone,[12)] α,α,α-trifluoroacetophenone,[13)] and thiobenzophenone.[7)] The intermediacy of the charge-transfer-type complex is also witnessed by facile reaction with amines.[3a,14)] That is, the photo-excited **1** does not abstract a hydrogen from ethanol, whereas it does in the presence of aniline, an electron-donor.

It is noteworthy that the excitation of **1** into the π,π^* state results in completely different reactivity from **1** in the n,π^* state.[15)] It is also interesting to compare the reactivity of **1** with that of thiobenzophenone, an aromatic thioketone, by the following two sets of reactions.[3a,12,16)]

$$\left\{\begin{array}{l} Ph_2C{=}S + EtOH \xrightarrow{h\nu} Ph_2\dot{C}SH + Me\dot{C}HOH \\ \qquad\qquad \longrightarrow Ph_2CHSH \xrightarrow{h\nu} Ph_2CHSSCHPh_2 \\ Bu^t_2C{=}S + EtOH \xrightarrow{h\nu} \text{no reaction} \end{array}\right.$$

$$\left\{\begin{array}{l} Ph_2C{=}S + PhCH_3 \overset{h\nu}{\rightleftharpoons} Ph_2CSH + PhCH_2\cdot \\ \qquad\qquad\qquad\qquad \longrightarrow \text{no reaction} \\ Bu^t_2C{=}S + PhCH_3 \xrightarrow{h\nu} Bu^t_2CSH + PhCH_2\cdot \\ \qquad\qquad \xrightarrow{PhCH_3} Bu^t_2CHSH + PhCH_2CH_2Ph \end{array}\right.$$

The results clearly suggest that, in their biradical-type excited states, thiobenophenone has more radical-character on sulfur than on thiocarbonyl-carbon, and the reverse is true for **1**. That is, the electronic configuration of thiocarbonyl group is much affected by the substituent. This is also true for their ground-state chemistry.[17)]

Experimental

Materials. Di-*t*-butyl thioketone (**1**) and thiobenzophenone were prepared as previously mentioned.[6,18)] Solvents were dried and distilled prior to the use.

Procedure. As a standard procedure, 300 mg of **1** in 10 ml of a hydrogen-donor solvent was sealed in a Pyrex tube (10 mmϕ) under an atmosphere of nitrogen. The mixture was irradiated with a 500 W high-pressure mercury lamp at a temperature of running water. After the reaction, the solvent was evaporated under a reduced pressure and the residual oil was subjected to column chromatography on silica gel with an eluent of hexane-benzene (4 : 1 v/v) mixture. The product isolated was identified to be 2,2,4,4-tetramethyl-3-pentanethiol by comparing the spectral data with those of the authentic sample.

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