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Di-*tert*-butyl Thioketone

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Synopsis. Di-*tert*-butyl thioketone, a new aliphatic thioketone, has been prepared and its IR and UV spectral properties are studied.

Chemistry of thiocarbonyl compounds has been described on the bases of information mostly obtained from studies on aromatic thioketones, thionesters, and thioamides,[1)] where the thiocarbonyl group is more or less resonance-participated by substituents. Information obtained from these compounds, therefore, may not be universal for the thiocarbonyl group and, before the description on the chemistry of thiocarbonyl compounds is generalized, it is desirable to study the chemistry of aliphatic thioketones.

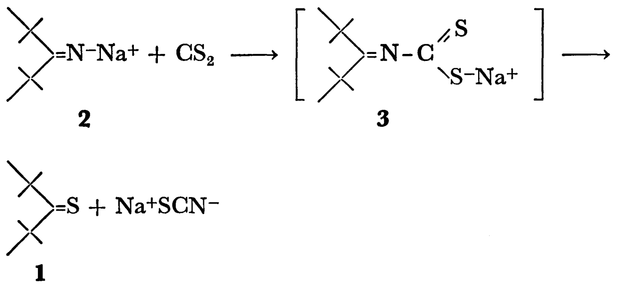
Aliphatic thioketones, however, have been the subject of little attention, because they are, generally, unstable. Namely, they are quite sensitive to air and, when possible, tautomerization to the corresponding enethiol is very fast.[1,2)]

In this article, we wish to report synthesis and spectral properties of di-*tert*-butyl thioketone, **1**.

General procedure to synthesize an aliphatic thioketone employs acid-catalyzed reaction of the corresponding ketal with hydrogen sulfide or, less frequently, the reaction of a ketone with phosphorous pentasulfide.[1,2a)] However, these procedures cannot be applied to the present system because of its inertness to S_N2-type reactions as well as difficulty to obtain the starting materials themselves.

Results and Discussion

Preparation. The thioketone, **1**, was prepared from sodium salt of di-*tert*-butyl ketimine, **2**[3)] and carbon disulfide after Ahmed and Lwowski.[4)] Since the intermediate, **3**, is stable enough to be dissolved in water, excess carbon disulfide and other organic impurities can be extracted with ether from the water layer before **3** decomposes to the final product. This procedure is more effective than fractional distillation to obtain **1** in high purity. That is, it is difficult to obtain the product in purity of higher than 97% after twice extractions and repeated fractional distillations, whereas repeated extractions (more than several times) until the water layer becomes colorless makes it possible to improve the purity as high as 99.9% by single fractional distillation. The purity was determined by vpc.



Although the overall yield of the reaction product is 34%, the yield of the thioketone by the addition of carbon disulfide to **2** can be calculated to be about 80%, since the yield of the latter compound is reported to be 43%.[3)] The reaction temperature should be kept below −10 °C during the addition of carbon disulfide in order to improve the yield of the thioketone.

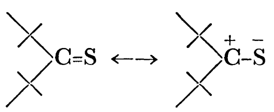
Detailed procedure will be described in Experimental Section.

Spectra. IR spectrum of **1** has an absorption at 1115 cm^{-1} due to $\nu_{C=S}$. The corresponding oxygen analog shows the absorption at 1686 cm^{-1} for $\nu_{C=O}$.[5)] The ratio, $\nu_{C=O}/\nu_{C=S}$, is 1.52. Thioacetone, isopropyl methyl thioketone, and diisopropyl thioketone, exibit their $\nu_{C=S}$ at 1269, 1250, and 1240 cm^{-1}, respectively,[6)] and their corresponding oxygen analogs show their $\nu_{C=O}$ at 1719,[7)] 1719,[7)] and 1716 cm^{-1},[5)] respectively. The ratios, $\nu_{C=O}/\nu_{C=S}$, for these pairs are 1.35—1.38. The value for pairs of aromatic thioketones and ketones also falls in this range.[8)] Thus, the frequency of the $\rangle$C=S stretching vibration in **1** is extraordinally shifted toward the value as low as those of thioamides (1140± 80 cm^{-1}),[9)] where the thiocarbonyl group has large single-bond character.[10)]

Absorption maxima in electronic spectra of **1** are listed in Table 1 together with those of other aliphatic thioketones so far reported.[11)]

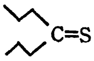
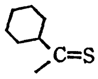
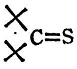
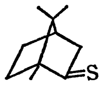
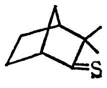
As has been recognized from the IR spectrum, the energy level of the C–S π-orbital in **1** is much higher than those of other thioketones, whereas the absorption maximum for the π-π^* transition of this thioketone appears at normal position. This fact indicates that the energy level of the C–S π^*-orbital in **1** is lifted up as high as that of the π-orbital. On the other hand, the energy for the n-π^* transition of **1** is much lower (1300 cm^{-1}) than those of other thioketones, which indicates that the energy level of the n-orbital is more lifted up than the π^*-orbital in this thioketone. This is an unusual phenomenon in the sense that the energy level of a π^*-orbital is more affected than that of an n-orbital by electronic nature of substituents in ketones[12)] and thioketones.[13)] Present results may suggest larger steric effect of *tert*-butyl groups in **1** than that in di-*tert*-butyl ketone.

The results, consequently, may be best interpreted by allotting the largest contribution of the canonical structure **1b** for the structure of **1**.[14)]



1a **1b**

Table 1. Electronic spectra of aliphatic thioketones

Thioketone	Solvent[a)]	n → σ		π → π*		n → π*	
		$\lambda_{\max}$, nm	ε	$\lambda_{\max}$, nm	ε	$\lambda_{\max}$, nm	ε
	E	313	5000	231	6200	492	7.9
	C	215	5100	230	6300	503	8.9
	E	214	5600	236	7400	492	9.1
	C	215	5900	236	7900	508	10.0
	E	—	—	237	7900	536	8.9
	C	—	—	237	7800	539	9.8
	E	210	3700	246	11000	481	10.5
	C	214	4200	244	11000	493	12.3
	E	212	3500	243	12000	479	10.7
	C	215	4000	240	10000	488	11.0

a) E, Ethanol: C, Cyclohexane.

Experimental

*Preparation of Di-*tert*-butyl Thioketone (**1**).* A suspension of 7 g (0.3 mol) of finely divided sodium metal in 50 ml of petroleum ether was stirred under an atmosphere of nitrogen, while 16.6 g (0.2 mol) of pivalonitrile was added to this suspension over a period of 1 hr. The temperature was kept between 25 and 30 °C. The mixture was stirred for additional 15 min and was filtered under an atmosphere of nitrogen to remove unreacted sodium. The filtrate was cooled with an ice-salt bath and stirred, while 10 ml of carbon disulfide was added dropwise over a period of 1 hr. When carbon disulfide is added dropwise to the solution of **2**, the yellow color of the solution turned from dark to pale. Stirring was continued for additional 2 hr at room temperature, then 150 ml of water was added and the mixture was washed with ether (80 ml × 5). The water layer was stood overnight at room temperature, whereas di-*tert*-butyl thioketone appeared as a red oil, which was separated from the water layer and the latter was extracted with ether. The red oil and the extract were combined and dried over calcium chloride. Distillation gave the thioketone (5.4 g) in 34% yield; bp 70.5—71.5 °C (18 Torr). NMR $\delta_{\mathrm{CCl_4}}^{\mathrm{TMS}}$ 1.43 (singlet).

Found: C, 67.85; H, 11.42; S, 20.50%. Calcd for $C_9H_{18}S$: C, 68.28; H, 11.46; S, 20.25%.

The purity of **1** was determined by vpc on Hitachi Perkin-Elmer F6 instrument (Golay column BDS 45 m, 80 °C, FID). The peak-area for **1** was compared to that of an unknown impurity contaminating.

Spectroscopy. The IR spectrum was recorded on Hitachi EPI-S2 with 2.5% CCl_4 solution. The electronic spectra were recorded on Shimadzu UV-200.

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14) Preliminary result from INDO-MO calculation supports the conclusion.