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Reaction of Electrochemically Generated Radical Anion of Thioketone with Alkylating Agents

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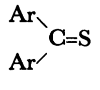
Synopsis. Electrochemically generated anion radicals of thioketones were allowed to react with alkyl halides (or tosylate). Electronic structure of the anion radical is discussed on the basis of the products.

It was reported that the polarization of thiocarbonyl group is largely affected by the substituent, and it is not uncommon that the dipole is oriented from positive sulfur to negative carbon.[1,2] It has also been proposed that the electronic structure of anion radical of thioketone reflects the electronic effect of the substituent; an anion radical from an aromatic thioketone being in carbanion-like structure, whereas that from an aliphatic thioketone being in thiolate-like structure.[3,4] However, the electronic structure of anion radical of thioketone is still ambiguous because the proposition bases on the behavior of transient reaction intermediate. Minoura and his co-worker reported the reactions of sodium thiobenzophenone thioketyl.[5] However, obviously the reaction does not represent the reaction of thiobenzophenone thioketyl since the anion radicals disproportionate easily into a dianion and a neutral molecule under the reaction conditions. At the same time, the anion radical from metal thioketyl is not free from large influence of the counter cation.[6] In order to understand intrinsic nature of anion radicals from thioketones, we generated them by cathodic reduction of thioketones, and studied their reactions with alkyl halides.

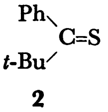
Results and Discussion

Appropriate amounts of thiobenzophenone (**1a**), 4,4′-dimethoxythiobenzophenone (**1b**), or thiopivalophenone (**2**) and an alkyl halide or tosylate were dissolved in acetonitrile and subjected to cathodic reduction (−1.6 V *vs.* SCE) in the presence of tetraethylammonium perchlorate as supporting electrolyte. After the color of thioketone had disappeared completely, reaction products were analyzed. Results are summarized in Table 1. Since the reduction potentials of **1** (≈−1.0 V *vs.* SCE) and **2** (≈−1.3 V *vs.* SCE) are lower than those of alkyl halides,[7] the electrochemical reduction may reduce thioketone rather than the alkyl halide. Initial reduction of thioketone is also supported by the fact that the reaction with **1** affords *C*-alkylated product(s); diaryl or aryl alkyl thioketone is known to be a very efficient free-radical scavenger,[8] and if the alkyl halide were the species to be reduced initially, all products should be *S*-alkylated ones. However, it is plausible that the anion radical of thioketone transfers an electron to the alkyl halide within a solvent cage when they encounter each other, as proposed for the reaction of thiolate anion and alkyl halide.[9]



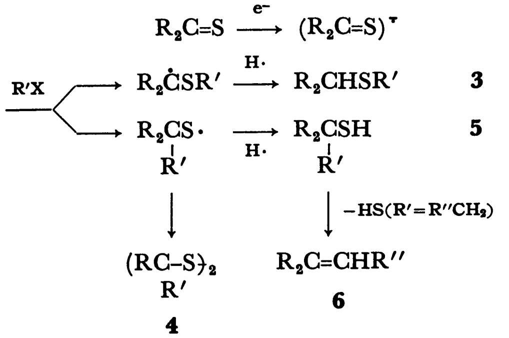
$Ar_2C{=}S$

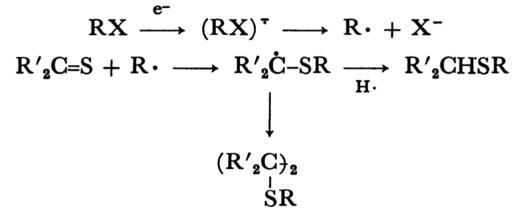
1a; Ar = C_6H_5
1b; Ar = p-$MeOC_6H_4$



$Ph(t\text{-}Bu)C{=}S$

2





$$R'_2C{=}S \xrightarrow{e^-} (R'_2C{=}S)^{\overline{\cdot}} \xrightarrow{RX} [(R'_2C{=}S)(RX)^{\overline{\cdot}}]_{cage}$$
$$\longrightarrow R'_2\dot{C}{-}SR + X^- \xrightarrow{H\cdot} R'_2CHSR + X^-$$

Although not major, the formation of *C*-alkylated product(s) from **1**, but not from **2**, suggests that the anion radical of diaryl thioketone has more carbanion-

Table 1. Isolated yields of products

Thioketone	Alkyl halide	Reaction time/min	Yield/%				
			S-Alkylated product, **3**	*C*-Alkylated product			Others
				4	**5**	**6**	
1a	MeI	50	20	6			18[a)]
	MeOTs[b)]	40	15	10			
	EtI	40	15	—[c)]			
1b	MeI	50	26		3	12	
	MeOTs[b)]	60	35		15	—[c)]	35[a)]
	EtI	30	24			14	
2[d)]	MeI	—[e)]	16				
	MeOTs[b)]	—[e)]	46				
	$PhCH_2Br$	—[e)]	10				
	i-PrBr	—[e)]	23				
	$BrCH_2$–CH_2CH_2Cl	—[e)]	27[f)]				

a) $Ar_2C{=}O$. b) Methyl *p*-toluenesulfonate. c) Trace amount. d) One mmol of **2** and 4 mmol of an alkyl halide were used. e) Overnight (≈20 h). f) *ω*-Chloro sulfide was obtained.

like character than alkyl aryl thioketone accordantly with the previous proposal.[2,3] Olefinic products are formed only when **1b** is subjected to the reaction, probably because electron-releasing effect of two *p*-methoxyl groups facilitates El-type elimination of hydrogen sulfide from the thiol resulted by *C*-alkylation.

It is interesting, in summary, to note that one can obtain *C*-alkylated product(s) when a neutral alkyl aryl or dialkyl thioketone is treated with a carbanion, whereas only *S*-alkylated product is obtained by the same reaction with diaryl thioketone.

Experimental

Materials. Thioketones were prepared according to the literature procedure.[10] Tetraethylammonium perchlorate, alkyl halides, and methyl tosylate were purchased from a commercial source (Nakarai Chem. Co.). Acetonitrile was distilled three times on phosphorus pentaoxide and once on potassium carbonate, then kept in a bottle filled with dry argon and capped by a silicon-rubber stopper.

Procedure. In both arms of a H-shaped electrolytic cell, each 5 cm^3 of acetonitrile containing 100 mg of tetraethylammonium perchlorate was placed. Then 0.25 mmol of a thioketone and 1 mmol of an alkyl halide (or tosylate) were dissolved in the cathode. Platinum electrodes were used. The reaction was run under a constant voltage of -1.6 V (*vs.* SCE) at room temperature. After the color of thioketone had disappeared, the solution in the cathode was taken out, quenched with water, and extracted three times with dichloromethane. The organic layer was washed once with saturated aqueous sodium chloride and dried over anhydrous sodium sulfate, then the solvent was removed *in vacuo*. The material thus obtained was chromatographed on a HPLC (silica gel) and product isolated were identified and quantitatively analyzed by NMR and mass spectroscopy.

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