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Phase Transfer Catalyzed Reaction of Organic Thiocyanates with Hydroxide Ion

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Synopsis. The reactions of 9-fluorenyl, phenacyl, benzhydryl, and benzyl thiocyanates (or the corresponding bromides with sodium thiocyanate) with hydroxide ion under phase transfer conditions afforded 9,9′-bifluorenylidene, 2,3-dibenzoylthiirane, thiobenzophenone and dibenzyl disulfide, respectively.

It is well known that carbanion-forming reactions are accelerated by cationic micelles.[1] Favored formation of carbanion is also known for phase transfer catalyzed reactions,[2] including our own works.[3–5] Recently, we have demonstrated that the mechanism of hydrolysis for esters bearing α-hydrogen changes from addition-elimination to elimination-addition mechanism under micellar conditions.[6] This finding has led us to check the reaction in the title.

In this paper, we describe the reactions of organic thiocyanates with hydroxide ion in the two-phase system, together with the reactions of the corresponding organic bromides with hydroxide ion in the presence of sodium thiocyanate, in the hope of finding a convenient method for the preparation of thiocarbonyl compounds.

Results and Discussion

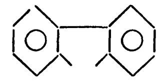
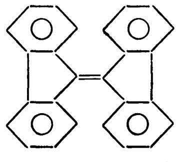
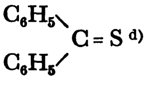
Thiocarbonyl compounds are usually prepared by the reaction of the corresponding carbonyl compounds or acetals with hydrogen sulfide in the presence of H^+ or by HCN elimination from organic thiocyanates with base.[7] In these reactions anhydrous conditions are usually required. The present reaction was carried out by stirring two phases of organic thiocyanates dissolved in CH_2Cl_2 or benzene and aqueous sodium hydroxide in the presence of hexadecyltrimethylammonium bromide (CTABr) as the phase transfer catalyst. Other catalysts, such as methyltrioctylammonium chloride and benzyltriethylammonium bromide, did not make much difference in the yields of products. The reactions could also be performed by using organic bromides and sodium thiocyanate to give the corresponding organic thiocyanates *in situ* during the reaction. The results are summarized in the Table.

The run 1 indicates the formation of 9,9′-bifluorenylidene in more than 90% yield. The same result was obtained by using 9-bromofluorene and sodium thiocyanate. Although 9-bromofluorene is known to give 9,9′-bifluorenylidene with base,[8] the present reaction was found to be much slower in the absence of sodium thiocyanate than in its presence. Thus, the reaction of 9-bromofluorene is considered to proceed through the formation of 9-thiocyanofluorene.

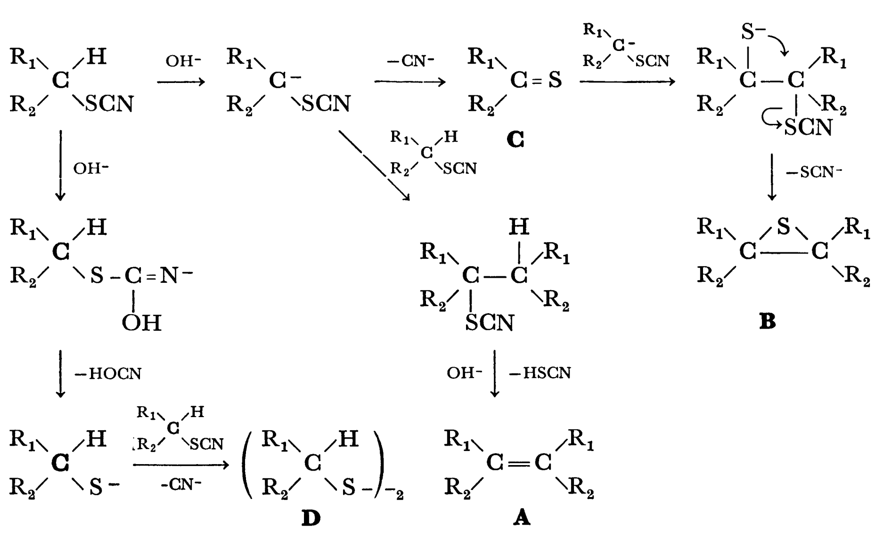
The episulfide obtained in the reaction of benzoylmethyl thiocyanate (run 2) is presumably the *trans*-isomer since *trans*-1,2-dibenzoylethylene was obtained on treatment of the episulfide with triphenylphosphine. In the case of benzhydryl thiocyanate (run 3) thiobenzophenone was obtained in a quantitative yield. Finally, dibenzyl thiocyanate gave disulfide (run 4).

These results may be tentatively accounted for by the following reaction scheme where **A**, **B**, **C**, and **D** stand for the products of runs 1—4, respectively.

TABLE 1. $R_1R_2CHSCN \xrightarrow[\text{CTABr, under } N_2]{\text{aq NaOH/}CH_2Cl_2\text{ or benzene}}$ Products

Run	R_1	R_2	Conditions			Products (yield)	
			[NaOH]	Temp	Time		
1			5 M[a]	r.t	2—3 h		(90—96%)
2	C_6H_5CO	H	5 M[a]	r.t	18 h	 $C_6H_5COCH—CHCOC_6H_5$ (bridged by S) Unidentified[c]	(37—45%)
3	C_6H_5	C_6H_5	15 M[b]	60—70 °C	2—3 days	 $(C_6H_5)_2C=S$[d]	(90%)
4	C_6H_5	H	15 M[a]	60—70 °C	24 h	$(C_6H_5CH_2S)_2$[e]	(30%)

a) With CH_2Cl_2. b) With benzene. c) This was found in the aqueous layer and precipitated by acidifying the solution. d) The absorption spectrum (λ_{max} 595 nm, $\varepsilon=167$ in *i*-PrOH)[10] indicated a quantitative yield. e) Starting material was recovered (65%).



Scheme 1.

Carbene coupling can be conceivable for the formation of **A**.9) However, no carbene adduct was obtained in the presence of cyclohexene or styrene. Episulfide (**B**) might be formed by the addition-elimination of SCN$^-$ to **A**. However, 1,2-dibenzoylethylene (**A**) did not give the episulfide of run 2 in the presence of NaSCN under the present reaction conditions. In the case of run 4 to form **D**, the benzyl methylene may not be active enough to form carbanion under the present phase transfer conditions.

The above reaction is highly dependent on the structure of substrate and does not appear to be generally useful for synthetic purposes except for the run 3. In the run 3, benzhydryl bromide or thiocyanate can be readily converted to the thioketone in a quantitative yield, and this method may be generally applicable to the synthesis of diaryl thioketone.

Experimental

All melting points are uncorrected. The thiocyanates were prepared from the corresponding bromides and sodium thiocyanate in dry acetone.10)

Phenacyl thiocyanate, mp 75 °C (from ether) (lit,11) mp 75—76 °C), 70%.

9-Fluorenyl thiocyanate, mp 118—119 °C (from benzene), 78%.

Benzhydryl thiocyanate, mp 35 °C (from ether)(lit,12) mp 35—36 °C), 93%. The other reagents were purchased from Tokyo Kasei Co.

Reaction of Thiocyanates with Hydroxide Ion under Phase Transfer Conditions. A mixture of the organic thiocyanate (10 mmol), CTABr (0.1 mmol) in CH_2Cl_2 (6 ml) and aqueous sodium hydroxide (2 ml) was stirred under N_2 atmosphere. The CH_2Cl_2 layer was separated and dried over Na_2SO_4. After CH_2Cl_2 was evaporated, the products were isolated by column chromatography (silica gel; benzene) for phenacyl and benzyl thiocyanates. 9,9′-Bifluorenylidene and 2,3-dibenzoylthiirane were isolated by recrystallization.

9,9′-Bifluorenylidene, mp 189—190 °C ($CHCl_3$–EtOH) (lit,13) mp 188 °C).

2,3-Dibenzoylthiirane, mp 77—77.5 °C (CH_2Cl_2–EtOH); NMR ($CDCl_3$) δ 4.00 (2H, s), 7.3—8.1 (10H). Found: C, 71.30; H, 5.00; S, 11.80%. Calcd for $C_{16}H_{12}O_2S$: C, 71.64; H, 4.47; S, 11.95%.

Reaction of the Bromides with a Mixture of Sodium Thiocyanate and Sodium Hydroxide under Phase Transfer Conditions. A mixture of the bromides (5 mmol), CTABr (0.1 mmol) in benzene (5 ml) and an aqueous solution containing equal amount of sodium thiocyanate and sodium hydroxide was stirred at a given temperature. The product isolation was performed with the same procedure as in the above reaction of thiocyanates.

Desulfurization of 2,3-Dibenzoylthiirane by Triphenylphosphine. A mixture of 2,3-dibenzoylthiirane 0.32 g (1.2 mmol) and triphenylphosphine 0.5 g (1.9 mmol) in 10 ml of xylene was refluxed overnight. Xylene was evaporated and the residue was subjected to column chromatography (silica gel; benzene). *trans*-1,2-Dibenzoylethylene was obtained (0.24 g, 85%), mp 109 °C (lit,14) mp 109—110 °C).

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