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The Preparation of Cyclic Dithia and Thiaza Compounds by the Reaction of Potassium Carbonate with Heterocumulenes and Alkylene Dibromides or Carbonate Catalyzed by Organostannyl Compounds

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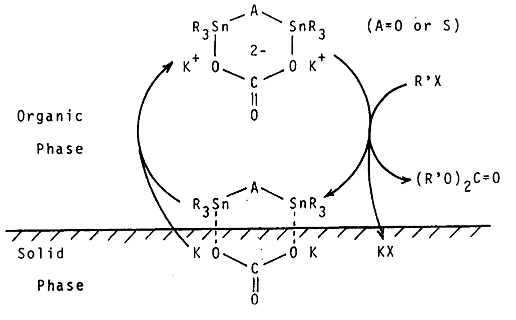
Cyclic 1,3-dithia- and 1,3-thiaza-2-ylidene compounds were obtained by the heterogeneous reaction of solid potassium carbonate, a sulfur-containing heterocumulene, such as aryl isothiocyanate, carbon disulfide, or carbonyl sulfide, and alkylene dibromides or ethylene carbonate in the presence of bis(tributylstannyl) compounds. The effect of an organostannyl catalyst on these reactions is discussed.

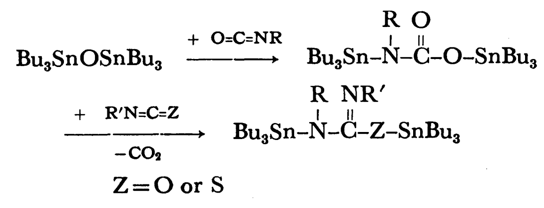
Alkali carbonates are usually insoluble in aprotic organic solvents and are generally used as weak bases in organic reactions. It was recently reported that potassium and sodium carbonates acted as strong bases for the generation of ylide[1] and carbanions[2] by means of a two-phase procedure catalyzed by a crown ether or quarternary salt. From the viewpoint of the further utilization of alkali carbonates other than a base, the fixation of carbonate ion into organic compounds is attractive, but all attempts to do so have been unsuccessful till lately; Soga[3] has reported that the polycarbonate was obtained by the reaction of potassium carbonate with α,α′-dibromo-*p*-xylene in the presence of a crown ether.

In a previous report,[4] we found that bis(tributylstannyl) compounds were effective two-phase catalysts for the heterogeneous nucleophilic reaction of solid potassium carbonate with alkyl bromides in polar aprotic solvents, affording dialkyl carbonates in good yields (Scheme 1).



Scheme 1. Preparation of dialkyl carbonates.

Exchange reactions between the CO_2 group in the dimetallocarbamate and heterocumulenes have been observed in organostannyl compounds (Eq. 1).[5]



$$\mathrm{Bu_3SnOSnBu_3} \xrightarrow{+\ \mathrm{O{=}C{=}NR}} \mathrm{Bu_3Sn{-}\overset{R}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}SnBu_3}$$

$$\xrightarrow[-\mathrm{CO_2}]{+\ \mathrm{R'N{=}C{=}Z}} \mathrm{Bu_3Sn{-}\overset{R}{N}{-}\overset{NR'}{\overset{\|}{C}}{-}Z{-}SnBu_3} \qquad (1)$$

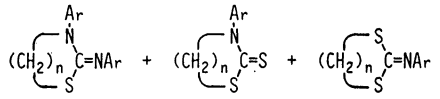
$Z{=}O$ or S

It is supposed that, analogously to Eq. 1, the stannate complex proposed for the soluble intermediate in Scheme 1 takes part in the exchange reactions of the CO_2 group in the ate-complex with various heterocumulenes. Also the stannate complexes resulting from the exchange reaction can be expected to give the corresponding heterocyclic compounds by cyclization with bifunctional alkylene compounds. On the basis of this working hypothesis, we wish to report here the use of organostannyl compounds in the activation of potassium carbonate in the preparation of cyclic 1,3-thiaza- and 1,3-dithia-2-ylidene compounds from sulfur-containing heterocumulenes and alkylene dibromides or ethylene carbonate. This procedure is carried out under mild conditions using an insoluble weak base, potassium carbonate, and does not require poisonous or awkward reagents.

Results and Discussion

Reaction of Potassium Carbonate with Aryl Isothiocyanates or Carbon Disulfide and Alkylene Dibromide. Anhydrous potassium carbonate, alkylene dibromide, two equivalents of aryl isothiocyanate, and hexabutyldistannathiane (5 mol%) were stirred for 8 h in refluxing acetonitrile under dry nitrogen to form 1,3-thiaza and 1,3-dithia compounds, **1**—**3**, accompanied by the elimination of carbon dioxide, carbonyl sulfide, and aryl isocyanate (Eq. 2). The carbonyl sulfide was trapped and confirmed by means of its IR spectrum.

$$K_2CO_3 + 2ArNCS + Br(CH_2)_nBr \xrightarrow{\text{Organostannyl catalyst}}$$



(2)

1a-c 2a-c 3a-c

a: Ar=Ph, n=2, b: Ar=p-Tol, n=2, c: Ar=Ph, n=3

From the reaction products, triaryl isocyanurate was isolated; it supported the elimination of aryl isocyanate in the reaction. The cyclic 3-aryl-2-arylimino-1,3-thiaza compound (**1**), 2-thioxo-1,3-thiaza compound (**2**), and 2-arylimino-1,3-dithia compound (**3**) were isolated and identified by their melting points and IR, NMR, and mass spectra. The results are summarized in Table 1.

From the results shown in Table 1, hexaalkyldistannoxane and -distannathiane can be seen to promote Reaction 2 distinctly. The reaction can scarcely

Table 1. Reactions of potassium carbonate, aryl isothiocyanates, and alkylene dibromides a)

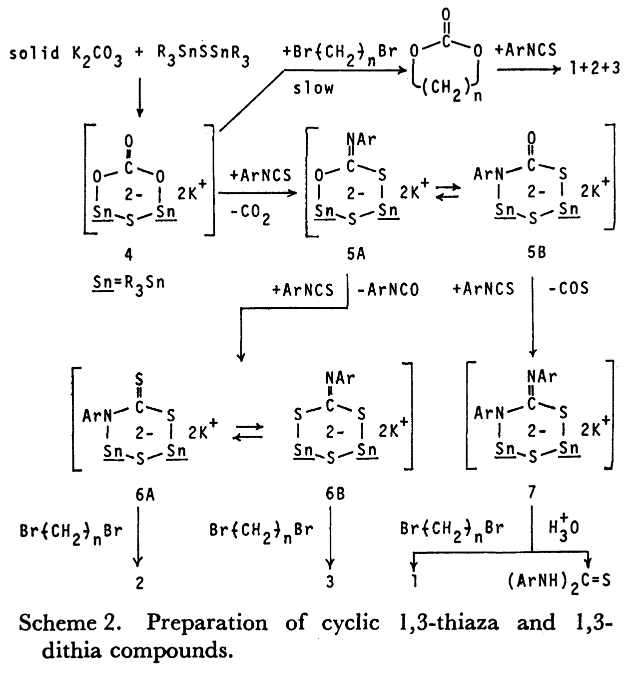
Ar in ArNCS	n in $Br(CH_2)_nBr$	Catalyst (mol%) b)	Reaction time/h	Product yield/% 1	2	3
Ph	2	None	4	5(**1a**)	Trace(**2a**)	Trace(**3a**)
Ph	2	Bu_2SnS(10)	4	26(**1a**)	12(**2a**)	8(**3a**)
Ph	2	$(Bu_3Sn)_2O$(5)	4	51(**1a**)	21(**2a**)	12(**3a**)
Ph	2	$(Bu_3Sn)_2S$(5)	4	48(**1a**)	17(**2a**)	15(**3a**)
Ph	2	$(Me_3Sn)_2S$(5)	4	41(**1a**)	17(**2a**)	13(**3a**)
Ph	2	Bu_3SnCl(10)	4	Trace(**1a**)	Trace(**2a**)	Trace(**3a**)
p-Tol	2	$(Bu_3Sn)_2O$(5)	24	35(**1b**)	18(**2b**)	18(**3b**)
Ph	3	$(Bu_3Sn)_2O$(5)	24	24(**1c**)	19(**2c**)	18(**3c**)

a) Reaction conditions: potassium carbonate (10 mmol), aryl isothiocyanate (20 mmol), alkylene dibromide (10 mmol), acetonitrile (10 ml), at the refluxing temperature. b) Based on the alkylene dibromide used.

proceed without the catalyst. However, dibutylstannathiane existing in a cyclic trimer6) is less effective, and chlorotributylstannane does not accelerate Reaction 2 at all, although it was an excellent catalyst like the bis(tributylstannyl) compounds in the preparation of dialkyl carbonates. In Reaction 2, hexabutyldistannoxane might be converted to the thiane derivative by a rapid reaction with aryl isothiocyanate.7)

Bis(tributylstannyl) compounds may act as two-phase catalysts, as is shown in Scheme 1. The bis(tributylstannyl) compounds interact with solid potassium carbonate to form an ate-complex **4**. Since potassium carbonate and 1,2-dibromoethane gave only a low yield (<5%) of ethylene carbonate (**8**) even in the presence of a bis(tributylstannyl) catalyst, under the same conditions, the products, **1**—**3**, cannot be considered to be formed *via* **8**. Therefore, the ate-complex **4** may react with aryl isothiocyanate in the first step to form the ate-complex **5** which further reacts with another molecule of isothiocyanate to form sulfur- and nitrogen-containing ate-complexes, **6A**, **6B**, and **7** (Scheme 2).

Although these ate-complexes have not been established, the mild hydrolysis of the reaction mixture of potassium carbonate with phenyl isothiocyanate in the presence of hexabutyldistannathiane gave *N*,*N'*-diphenylthiourea which suggests the formation of **7**.



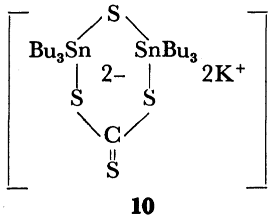
Scheme 2. Preparation of cyclic 1,3-thiaza and 1,3-dithia compounds.

The reaction *via* the ate-complexes **4**—**7** will be the same type of reaction as in the case of a heterocumulene exchange reaction (1) using neutral bis(tributylstannyl) compounds.

The ate-intermediates **6A** and **7** have reactive Sn–N sites and react with alkylene dibromide to afford **1** or **2**. On the other hand, **6B** has no Sn–N site but a less reactive Sn–S site, and the yield of **3**, which may be expected to be a major product from the dithiocarbamate dianion because of the large nucleophilicity of its S$^-$ site,8) is lower than that of **2**.

Hexabutyldistannathiane is inert in many reactions of organostannyl compounds, such as Reaction 1,5) but in Reaction 2 this compound is highly active. This activity of hexabutyldistannathiane may be ascribed to the formation of ate-complexes.

Contrary to the reaction of aryl isothiocyanate, the reaction of carbon disulfide with potassium carbonate and 1,2-dibromoethane in acetonitrile for 12 h at reflux gave 1,3-dithiolane-2-thione (**9**) in a 90% yield, even in the absence of an organostannyl compound. Potassium trithiocarbonate from carbon disulfide and potassium carbonate is conceived of as the reactive intermediate because of its strong nucleophilicity. Futhermore, the tin atom in organostannyl compounds shows a strong affinity to the sulfur atom serving to stabilize the trithiocarbonate anion by the formation of the ate-complex **10**. This may explain the lowering of the yield of **9** down to 68% by the presence of hexabutyldistannathiane.



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Reaction of Potassium Carbonate with Heterocumulenes and Ethylene Carbonate. When ethylene carbonate (**8**) is used instead of dibromoethane in the above reactions, the displacement of the CO_2 group in **8** by other hetero-

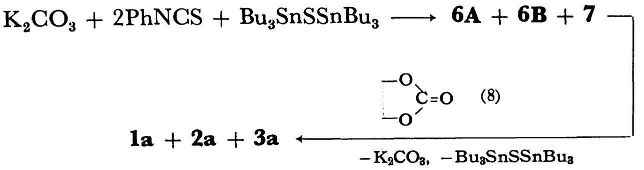
TABLE 2. REACTIONS OF ETHYLENE CARBONATE WITH VARIOUS HETEROCUMULENES CATALYZED BY HEXABUTYLDISTANNATHIANE AND/OR POTASSIUM CARBONATE[a)]

Heterocumulene used	Catalyst (mol%)[b)]			Reaction time/h	Solvent	Main product	Yield %
	K_2CO_3	$(Bu_3Sn)_2S$	18-Crown-6				
PhNCS	0	0	0	24	MeCN	—	0
PhNCS	5	0	0	24	MeCN	**3a**	28
PhNCS	5	5	0	24	MeCN	**3a**	50[c)]
PhNCS	5	5	0	24	C_6H_6	—	0
PhNCS	5	5	10	24	C_6H_6	**3a**	49
PhNCS	5	5	10	1	C_6H_6	**3a**	23
PhNCS	5	0	10	1	C_6H_6	**3a**	9
CS_2[d)]	5	0	0	24	MeCN	**9**	0
CS_2[d)]	5	5	0	24	MeCN	**9**	Trace
CS_2[d)]	5	5	10	24	MeCN	**9**	17
COS[d)]	5	0	0	48	MeCN	**11**	40
COS[d)]	5	5	0	48	MeCN	**11**	42

a) Ethylene carbonate (10 mmol), heterocumulene (20 mmol or more), and catalysts were heated in the solvent at reflux. b) Based on ethylene carbonate used. c) Accompanied by the formation of **1a** (11%) and **2a** (34%). d) In an autoclave at 80 °C.

cumulenes can be expected.

These heterocyclic compounds, **1a**, **2a**, and **3a**, were obtained in the reaction of **8** with phenyl isothiocyanate in refluxing acetonitrile using 5 mol% of potassium carbonate and hexabutyldistannathiane (Eq. 3). Contrary to Reaction 1, the main product was **3a** (not **1a**).[9)]

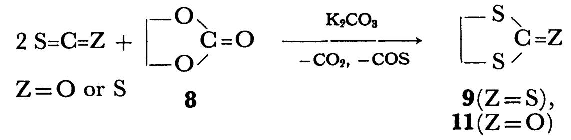


(3)

Potassium carbonate is reproduced in Reaction 3 so that the carbonate can act as a catalyst. Therefore, the activity of the organostannyl compound as a two-phase catalyst for solid potassium carbonate is less in the catalytic reaction (3) than that in the stoichio reaction (2) of the carbonate.

In a less polar solvent such as benzene, a mixed catalyst system of the distannathiane and 18-Crown-6 was found to be more effective in Reaction 3 as well as in the reaction for the preparation of dialkyl carbonates.[4)]

The analogous reaction of **8** with carbon disulfide or carbonyl sulfide, catalyzed by potassium carbonate in an autoclave at 80 °C, gave **9** and 1,3-dithiolane-2-one (**11**) respectively (Eq. 4).



(4)

The organostannyl catalyst was not effective either in the reaction with carbon disulfide or in that with carbonyl sulfide (Table 2). This can be also explained similarly by the strong Sn–S interaction in the proposed ate-complexes consisting of CS_3^{2-} and COS_2^{2-} as was described about that for **10**.

The attempted analogous reactions using phenyl isocyanate or di-*o*-tolylcarbodiimide, which contains no sulfur atom, gave no corresponding heterocyclic compounds.

Experimental

All the melting points were determined on a micro hot stage and were not corrected. The IR spectra were taken on a JASCO IR A-1 or A-3 spectrometer. The NMR spectra were recorded on a Hitachi R-24 spectrometer. The mass spectra were measured on a Hitachi RMU-7M spectrometer. Commercial potassium carbonate was dried at about 300 °C before use. The other reagents and solvents were dried by the usual methods. All the procedures were carried under a dry nitrogen atmosphere.

Reactions of Potassium Carbonate, Aryl Isothiocyanate, and Alkylene Dibromide. Potassium carbonate (10 mmol), phenyl isothiocyanate (10 mmol), and hexabutyldistannathiane (0.5 mmol) were stirred in refluxing acetonitrile (10 ml) for 8 h. Carbonyl sulfide thus evolved was trapped at −78 °C and identified by means of its IR spectrum (ν_{COS} 2038 cm^{-1}). After the reaction mixture had been filtered to remove the inorganic salts and acetonitrile had been evaporated *in vacuo*, hot diethyl ether was added to precipitate triphenyl isocyanurate: mp 283—287 °C (lit,[10)] 285—286 °C); IR (KBr) 1700 cm^{-1} (C=O). The ether solution was cooled to precipitate 3-phenyl-2-phenylimino-1,3-thiazolidine (**1a**, 48%), contaminated with a small amount of triphenyl isocyanurate, which was removed by recrystallization from diethyl ether. The solvent was evaporated from the ether solution, and then 3-phenyl-1,3-thiazolidine-2-thione (**2a**, 17%) and 2-phenylimino-1,3-dithiolane (**3a**, 15%) were isolated by column chromatography on silica gel (chloroform). **1a**: mp 135—137 °C (lit,[11)] 136—137 °C); IR ($CHCl_3$) 1628 cm^{-1} (C=N); NMR ($CDCl_3$) δ 3.15 (2H, t, J=6.6 Hz, SCH_2), 4.04 (2H, t, J=6.6 Hz, NCH_2), and 6.8—7.6 (10H, m, arom.); MS *m/e* 254 (M^+). **2a**: mp 132—134 °C (lit,[12)] 133—134 °C); IR ($CHCl_3$) 1260 cm^{-1} (C=S); NMR ($CDCl_3$) δ 3.40 (2H, t, J=7.6 Hz, SCH_2), 4.42 (2H, t, J=7.6 Hz, NCH_2), and 7.35 (5H, s, arom.); MS *m/e* 195 (M^+). **3a**: mp 42—44 °C (lit,[13)] 47—48 °C); IR ($CHCl_3$) 1592 cm^{-1} (C=N), NMR ($CDCl_3$) δ 3.36 (4H, s, SCH_2CH_2S) and 6.7—7.4 (5H, m, arom.);

MS *m*/*e* 195 (M^+).

Similarly, other heterocyclic compounds were obtained. Their yields, melting points, and spectral data were as follows: 3-*p*-Tolyl-2-*p*-tolylimino-1,3-thiazolidine (**1b**): 35%; 107—109 °C (lit,[11] 110 °C); IR ($CHCl_3$) 1629 cm^{-1} (C=N); NMR ($CDCl_3$) δ 2.29 (6H, s, CH_3), 3.16 (2H, t, J=6.6 Hz, SCH_2), 4.02 (2H, t, J=6.6 Hz, NCH_2), and 6.7—7.5 (8H, m, arom.); MS *m*/*e* 310 (M^+). 3-*p*-Tolyl-1,3-thiazolidine-2-thione (**2b**): 18%, 123—125 °C (lit,[12] 126 °C); IR ($CHCl_3$) 1263 cm^{-1} (C=S); NMR ($CDCl_3$) δ 2.36 (3H, s, CH_3), 3.42 (2H, t, J=7.7 Hz, SCH_2), 4.44 (2H, t, 7.7 Hz, NCH_2), and 7.28 (4H, s, arom.); MS *m*/*e* 209 (M^+). 2-*p*-Tolylimino-1,3-dithiolane (**3b**): 12%; oil (lit,[13] oil); IR ($CHCl_3$) 1580 cm^{-1} (C=N); NMR ($CDCl_3$) δ 2.32 (3H, s, CH_3), 3.51 (4H, s, SCH_2CH_2S), and 6.8—7.3 (4H, m, arom.); MS *m*/*e* 209 (M^+). 3-Phenyl-2-(phenylimino)perhydro-1,3-thiazine (**1c**): 24%; 139—141 °C (lit,[10] 139 °C); IR ($CHCl_3$) 1623 cm^{-1} (C=N); NMR ($CDCl_3$) δ 2.24 (2H, m, C–CH_2–C), 3.17 (2H, t, J=6.1 Hz, SCH_2), 3.77 (2H, t, 5.5 Hz, NCH_2), and 6.9—7.5 (10H, m, arom.), MS *m*/*e* 268 (M^+). 3-Phenylperhydro-1,3-thiazine-2-thione (**2c**): 19%, 105—106 °C; IR ($CHCl_3$) 1232 cm^{-1} (C=S); NMR ($CDCl_3$) δ 2.40 (2H, m, C–CH_2–C), 3.12 (2H, t, J=6.1 Hz, SCH_2), 3.82 (2H, t, J=5.5 Hz, NCH_2), and 7.2—7.5 (5H, m, arom.); MS *m*/*e* 209 (M^+). 2-Phenylimino-1,3-dithiane (**3c**): 18%; 113—116 °C (lit,[14] 117—118 °C); IR ($CHCl_3$) 1570 cm^{-1} (C=N); NMR ($CDCl_3$) δ 2.17 (2H, m, C–CH_2–C), 3.12 (2H, t, J=6.8 Hz, SCH_2), and 6.7—7.5 (5H, m, arom.); MS *m*/*e* 209 (M^+).

A reaction mixture from potassium carbonate, phenyl isothiocyanate, and hexabutyldistannathiane (5 mol%), obtained under the conditions described above, was hydrolyzed by the addition of dilute hydrochloric acid after the solvent had been evaporated; the residue was washed with hexane to remove the unreacted phenyl isothiocyanate. A small amount of a water-insoluble precipitate was obtained. By recrystallization from ethanol, *N*,*N*′-diphenylurea was isolated: mp 149—152 °C (lit,[15] 154 °C); IR (KBr) 1445 cm^{-1}.

Reaction of Ethylene Carbonate (8) with Phenyl Isothiocyanate. Ethylene carbonate (10 mmol), phenyl isothiocyanate (20 mmol), potassium carbonate (0.5 mmol), and hexabutyldistannathiane (0.5 mmol) were stirred in refluxing acetonitrile (10 ml). After the reaction mixture had then been treated as above, **1a** (11%), **2a** (34%), and **3a** (50%) were obtained. By an analogous reaction catalyzed by potassium carbonate (5 mol%), hexabutyldistannathiane (5 mol%), and 18-crown-6 (10 mol%) in refluxing benzene for 24 h, **1a** (16%), **2a** (24%), and **3a** (49%) were obtained.

Reaction of Ethylene Carbonate (8) with Carbon Disulfide or Carbonyl Sulfide. Ethylene carbonate (**8**, 20 mmol), carbon disulfide (40 mmol), potassium carbonate (1 mmol), hexabutyldistannathiane (1 mmol), and 18-crown-6 (2 mmol) were heated in a glass autoclave for 24 h at 80 °C. 1,3-Dithiolane-2-thione (**9**) was then isolated in a 17% yield by means of column chromatography.

By a similar procedure, the reaction of **8** (20 mmol) with carbonyl sulfide (40 mmol), catalyzed by potassium carbonate (1 mmol) and hexabutyldistannathiane (1 mmol) for 48 h at 80 °C, gave 1,3-dithiolane-2-thione (**11**, 42%) and **9** (2%). **11**: mp 31—33 °C (lit, [15] 35 °C); IR ($CHCl_3$) 1716 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.77 (4H, s, SCH_2CH_2).

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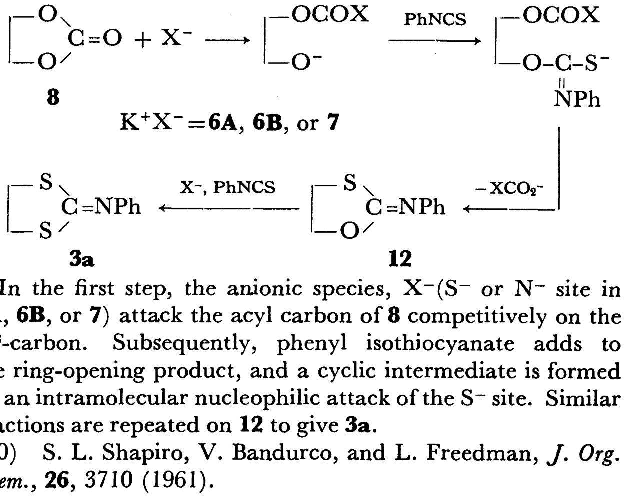
8) We obtained more **3a** (43%) than **2a** (17%) by the reaction of dibromoethane with $PhN(Li)CS_2Li$, which had been prepared *in situ* from aniline, butyllithium, and carbon disulfide; S. Sakai, N. Otani, and T. Fujinami, unpublished.

9) The reason for the formation of **3a** as the main product in Reactions 3 is not yet clear. However, we tentatively consider the reaction scheme to be as follows.



In the first step, the anionic species, X^-(S^- or N^- site in **6A**, **6B**, or **7**) attack the acyl carbon of **8** competitively on the sp^3-carbon. Subsequently, phenyl isothiocyanate adds to the ring-opening product, and a cyclic intermediate is formed by an intramolecular nucleophilic attack of the S^- site. Similar reactions are repeated on **12** to give **3a**.

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