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THE REACTION OF 2*H*-THIIN DERIVATIVES WITH PERACID. RING CONTRACTION AND ALKOXYLATION REACTIONS

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The cycloaddition reaction of aromatic thioketones (aryl naphthyl thioketones and 2-benzofuryl phenyl thioketone) with 2-chloroacrylonitrile followed by elimination of hydrogen chloride gave some 2*H*-thiin derivatives. The products reacted with MCPBA and an alcohol to afford ring-contracted product and alkoxylated derivatives.

Previously, we found that the cycloadducts obtained by the reaction of aryl 2-furyl or 2-thienyl thicketones with 2-chloroacrylonitrile readily eliminated hydrogen chloride in the presence of triethylamine to give o-quinodimethane-type derivatives of furan <u>1</u> or thicphene <u>2</u>.¹⁾ These compounds are extremely stable in contrast with usual o-quinodimethane-type compounds, ²⁻⁴⁾ and their high stability could be ascribed to mesomeric effect of the cyano group and sulfur atom. It has been presumed that conversion of sulfide-sulfur in the 2*H*-thiin ring of <u>1</u> and <u>2</u> to sulfoxide would bring marked change in the chemical properties of these compounds. Accordingly, some other structually related compounds were prepared and their reaction with MCPBA was examined.

Reactions of 1-naphthyl phenyl thioketone $(\underline{3})$, mesityl 2-naphthyl thioketone $(\underline{4})$, *p*-methoxyphenyl 2-naphthyl thioketone $(\underline{5})$, and 2-benzofuryl phenyl thioketone $(\underline{6})$ with 2-chloroacrylonitrile and triethylamine were carried out according to the previously described procedure¹⁾ and the corresponding 2*H*-thiin derivatives $(\underline{7}) - (\underline{10})$ were obtained, respectively. The results are presented in Table 1.



2-chloroacrylonitrile and triethylamine								
Thioketone	Product	Reaction time	Mp/°C	Yield/% ^{a)}				
3	7	3 h	170-172	61				
4	8	2 h	131 - 132	58				
<u>5</u>	<u>9</u>	2 h	161-164	73				

5 min

126-128

82

Table 1. The reaction of aromatic thicketones with

a) Based on the thicketone.

To $\underline{8}$ (5 mmol) dissolved in 40 cm³ dichloromethane a solution of MCPBA (5 mmol in 40 cm³ dichloromethane) was added dropwise with stirring at 0 °C under an atmosphere of dry nitrogen. Addition was completed within 1 h. The color of the solution turned from deep red to faint yellow. The solution was washed with saturated aqueous sodium hydrogencarbonate and dried over anhydrous sodium sulfate. Two products were formed as evidenced by TLC analysis. However, only one product was isolated by column chromatography on silica gel. This was not the expected sulfoxide but found to be 1-cyano-3-mesitylnaphtho-[1,2-c]thiophene (<u>11</u>). Thus, the ring contraction of <u>8</u> took place during the reaction. The other product checked by TLC analysis decomposed during separation by column chromatography. Accordingly, the mixture of two products was submitted to fractional recrystallization from methanol. Precipitates separated out on standing the solution for 2-3 days were found to be 2-methoxy derivatives of <u>8</u>, 1-cyano-4-mesityl-2-methoxy-2*H*-naphtho[2,1-*c*]thiin (<u>12a</u>). In this procedure, 11 was obtained from the filtrate.



 $\underline{13}$, Ar=p-MeOC₆H₄



<u>b</u>, Ar=Mesityl, R=Et <u>14a</u>, Ar=p-MeOC₆H₄, R=Me

The structures of <u>11</u> and <u>12a</u> were confirmed by the IR, mass, and ¹H NMR spectra and elemental analysis. The IR spectrum (KBr) of <u>11</u> showed a band at 2200 cm⁻¹ due to the cyano group. The mass spectrum (70 eV) showed ion peaks at m/z 327 (M⁺, 100), 312 (8), 310 (9), and 296 (12). The ¹H NMR spectrum (CDCl₃, 100 MHz) showed signals at δ 2.00 (s, 6H, CH₃), 2.37 (s, 3H, CH₃), 6.88 (d, $J_{4,5}$ = 9.3 Hz, 1H, H-4), 6.98 (broad s, 2H, C₆<u>H</u>₂Me₃), 7.28 (d, $J_{4,5}$ =9.3 Hz, 1H, H-5), 7.48-7.78 (m, 3H, aromatic protons), and 9.02-9.18 (m, 1H, H-9). The IR spectrum of <u>12a</u> showed a band at 2195 cm⁻¹ due to the cyano group. The mass spectrum showed a molecular ion peak at m/z 371 and base ion peak at m/z 340 (M⁺ - OCH₃). In the ¹H NMR spectrum, three singlets at δ 1.88 (3H), 2.25 (3H), and 2.32 (3H)

are assigned to methyl hydrogens of the mesityl group. Two singlets at δ 3.42 (3H) and 5.24 (1H) are assigned to methoxy hydrogens and H-2, respectively. Two doublets at δ 6.30 (1H) and 6.54 (1H) [$J_{5,6}$ =9.6 Hz] are assigned to olefinic protons of H-5 and H-6, respectively. Two broad singlets at δ 6.85 (1H) and 6.94 (1H) are assigned to aromatic protons in the mesityl group, and two multiplets at δ 7.20-7.45 (3H) and 8.82-9.08 (1H) are assigned to the other aromatic protons. These data are consistent with the proposed structures <u>11</u> and <u>12a</u>.



Similarly, treatment of <u>9</u> or <u>10</u> with MCPBA followed by the addition of an alcohol gave the corresponding ring-contracted product <u>13</u> or <u>15</u> and alkoxylated derivative <u>14</u> or <u>16</u>, respectively. On the other hand, the reaction of <u>7</u> gave only alkoxylated product <u>17</u>. 3-Cyano-4,6-diphenyl-2*H*-thiin (<u>18a</u>), a simple 2*H*-thiin derivative, obtained by the reaction of thiochalcone with 2-chloroacrylo-nitrile,⁵) reacted with MCPBA and an alcohol to give only ring-contracted compound, 2-cyano-3,5-diphenylthiophene (<u>19a</u>).



<u>18a</u>, Ar=Ph <u>b</u>, Ar=p-MeOC₆H₄ <u>19a</u>, Ar=Ph <u>b</u>, Ar=p-MeOC₆H₄ $\int_{S}^{CN} Ar$

b, Ar=Mesityl

Table 2. The reaction of 2H-thiin derivatives with MCPBA and ROH							
Entry	2 <i>H−</i> Thiin	Ar	Product	R	Yield/%	Mp/°C	
1	7	-	<u>17a</u>	Me	41	183-185	
2	<u>7</u>	-	<u>17b</u>	Et	39	127-129	
3	8	mesityl	$\int \underline{11}$	-	34	138-140]	
			<u>12a</u>	Me	60	185-187	
4	8	mesityl	<u> 11</u>	-	16	138-140	
			<u>12b</u>	Et	80	176-178	
5	9	p-MeOC ₆ H ₄	13	-	20	210-213	
			<u>14a</u>	Me	25	175-177	
6	10	-	<u>15</u>	-	14	169-170	
			<u> 16a</u>	Me	60	126-128	
7	<u>18a</u>	Ph	<u>19a</u>	-	18	125-127	
8	<u>18b</u>	$p-MeOC_6H_4$	<u>19b</u>	-	53	132-134	
9	<u>2a</u>	Ph	<u>20a</u>	-	5	141-143	
10	<u>2b</u>	mesityl	<u>20b</u>	-	53	131-133	

The reaction of <u>la</u> or <u>lb</u> with MCPBA under similar reaction conditions gave only unidentified decomposition product. When <u>2a</u> or <u>2b</u> was treated with MCPBA and an alcohol, two products were formed as indicated by TLC, respectively, but only the ring-contracted product <u>20a</u> or <u>20b</u> was isolated. The results are presented in Table 2.

As shown in Scheme 1, alkoxylated product $\underline{25}$ is surmised to be formed via the Pummerer-type rearrangement of sulfoxide $\underline{22}$. The ready reaction under mild reaction conditions may be ascribable to the presence of the electron-withdrawing cyano group at the β -position of $\underline{22}$,⁶⁾ and the nucleophilic attack of the alcohol would take place to the thiinylium cation $\underline{24}$ to produce $\underline{25}$.^{7,8)} On the other hand, the ring contraction of 2H-thiin derivative $\underline{21}$ is an unusual and interesting reaction.⁹⁾ It is plausible that the sulfoxide $\underline{22}$ or its protonated species $\underline{23}$ undergoes an intramolecular rearrangement and subsequent elimination of formaldehyde to give $\underline{26}$. However, experimental information has not been obtained to support the mechanism.



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