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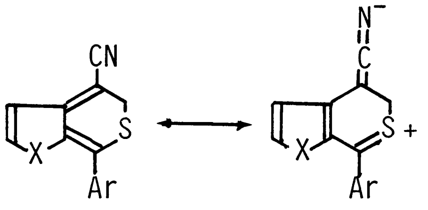
THE REACTION OF 2*H*-THIIN DERIVATIVES WITH PERACID. RING CONTRACTION AND ALKOXYLATION REACTIONS

Haruo OHMURA and Shinichi MOTOKI*
Department of Chemistry, Faculty of Science, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162

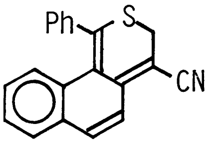
The cycloaddition reaction of aromatic thioketones (aryl naphthyl thioketones and 2-benzofuryl phenyl thioketone) with 2-chloroacrylonitrile followed by elimination of hydrogen chloride gave some 2*H*-thiin derivatives. The products reacted with MCPBA and an alcohol to afford ring-contracted product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

Previously, we found that the cycloadducts obtained by the reaction of aryl 2-furyl or 2-thienyl thioketones with 2-chloroacrylonitrile readily eliminated hydrogen chloride in the presence of triethylamine to give *o*-quinodimethane-type derivatives of furan 1 or thiophene 2.[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 1 and 2 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 (3), mesityl 2-naphthyl thioketone (4), *p*-methoxyphenyl 2-naphthyl thioketone (5), and 2-benzofuryl phenyl thioketone (6) with 2-chloroacrylonitrile and triethylamine were carried out according to the previously described procedure[1)] and the corresponding 2*H*-thiin derivatives (7)-(10) were obtained, respectively. The results are presented in Table 1.



1a, X=O, Ar=Ph
b, X=O, Ar=Mesityl
2a, X=S, Ar=Ph
b, X=S, Ar=Mesityl
c, X=S, Ar=*p*-ClC_6H_4



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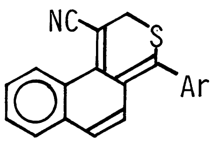

8, Ar=Mesityl
9, Ar=*p*-$MeOC_6H_4$

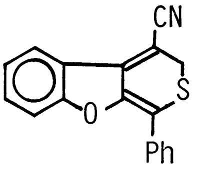

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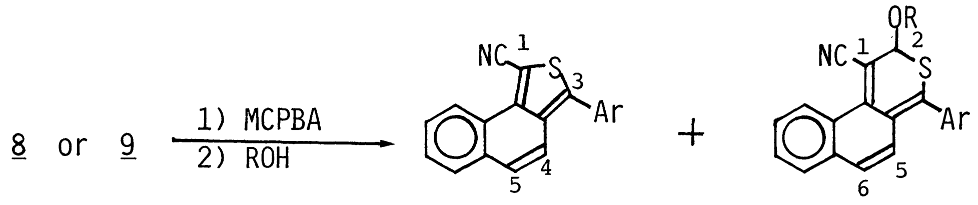
Table 1. The reaction of aromatic thioketones with 2-chloroacrylonitrile and triethylamine

Thioketone	Product	Reaction time	Mp/°C	Yield/%[a)]
3	7	3 h	170-172	61
4	8	2 h	131-132	58
5	9	2 h	161-164	73
6	10	5 min	126-128	82

a) Based on the thioketone.

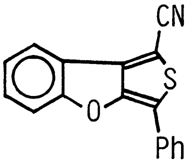
To 8 (5 mmol) dissolved in 40 cm^3 dichloromethane a solution of MCPBA (5 mmol in 40 cm^3 dichloromethane) was added dropwise with stirring at 0 °C under an atmosphere of dry nitrogen. Addition was completed within 1 h. The color of the solution turned from deep red to faint yellow. The solution was 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 (11). Thus, the ring contraction of 8 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 8, 1-cyano-4-mesityl-2-methoxy-2*H*-naphtho[2,1-*c*]thiin (12a). In this procedure, 11 was obtained from the filtrate.



11, Ar=Mesityl
13, Ar=*p*-MeOC$_6$H$_4$

12a, Ar=Mesityl, R=Me
b, Ar=Mesityl, R=Et
14a, Ar=*p*-MeOC$_6$H$_4$, R=Me

The structures of 11 and 12a were confirmed by the IR, mass, and ^{1}H NMR spectra and elemental analysis. The IR spectrum (KBr) of 11 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 ^{1}H NMR spectrum (CDCl$_3$, 100 MHz) showed signals at δ 2.00 (s, 6H, CH$_3$), 2.37 (s, 3H, CH$_3$), 6.88 (d, $J_{4,5}$= 9.3 Hz, 1H, H-4), 6.98 (broad s, 2H, $C_6\underline{H}_2Me_3$), 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 12a 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$^+$ - OCH$_3$). In the ^{1}H 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 11 and 12a.



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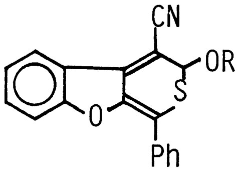
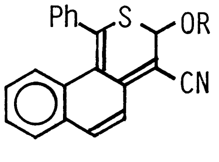
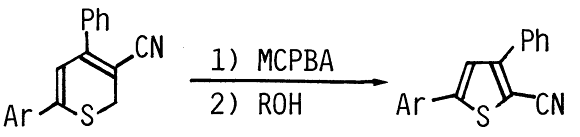


16a, R=Me



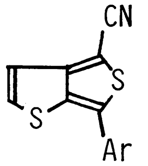
17a, R=Me
b, R=Et

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



18a, Ar=Ph
b, Ar=*p*-MeOC$_6$H$_4$

19a, Ar=Ph
b, Ar=*p*-MeOC$_6$H$_4$



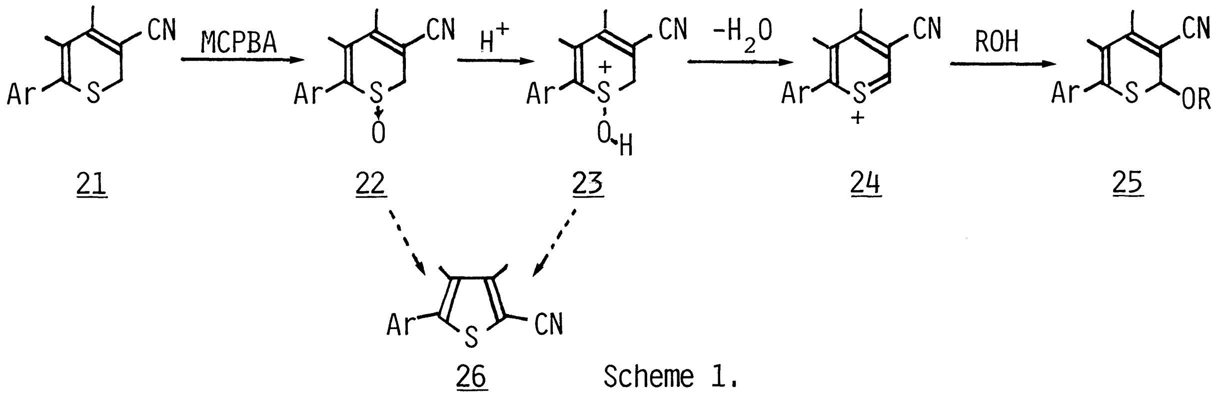
20a, Ar=Ph
b, Ar=Mesityl

Table 2. The reaction of 2*H*-thiin derivatives with MCPBA and ROH

Entry	2*H*-Thiin	Ar	Product	R	Yield/%	Mp/°C
1	7	-	17a	Me	41	183-185
2	7	-	17b	Et	39	127-129
3	8	mesityl	11	-	34	138-140
			12a	Me	60	185-187
4	8	mesityl	11	-	16	138-140
			12b	Et	80	176-178
5	9	*p*-MeOC$_6$H$_4$	13	-	20	210-213
			14a	Me	25	175-177
6	10	-	15	-	14	169-170
			16a	Me	60	126-128
7	18a	Ph	19a	-	18	125-127
8	18b	*p*-MeOC$_6$H$_4$	19b	-	53	132-134
9	2a	Ph	20a	-	5	141-143
10	2b	mesityl	20b	-	53	131-133

The reaction of 1a or 1b with MCPBA under similar reaction conditions gave only unidentified decomposition product. When 2a or 2b was treated with MCPBA and an alcohol, two products were formed as indicated by TLC, respectively, but only the ring-contracted product 20a or 20b was isolated. The results are presented in Table 2.

As shown in Scheme 1, alkoxylated product 25 is surmised to be formed *via* the Pummerer-type rearrangement of sulfoxide 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 22,[6)] and the nucleophilic attack of the alcohol would take place to the thiinylium cation 24 to produce 25.[7,8)] On the other hand, the ring contraction of 2*H*-thiin derivative 21 is an unusual and interesting reaction.[9)] It is plausible that the sulfoxide 22 or its protonated species 23 undergoes an intramolecular rearrangement and subsequent elimination of formaldehyde to give 26. However, experimental information has not been obtained to support the mechanism.



Scheme 1.

References

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8) In the course of the investigation, a similar reaction was reported. R. Masuda, M. Hojo, Y. Mochizuki, M. Yokota, and E. Okada, 49th National Meeting of the Chemical Society of Japan, Tokyo, April 1984, Abstr., No. 1F01.
9) For other ring contraction reactions of thiins, see, H. C. Van der Plas, "Ring Transformations of Heterocycles," Academic Press, London (1973), Vol. 2, Chap. 4, pp. 48-57.

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