Research Reports of Oyama National
College of Technology, No.31(1999), 141－146

One-Pot Synthesis of 1, 2-Dithiolane Derivatives from Thiocyanatoacetophenone and Some Aromatic Aldehydes

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The title compounds, 3, 5-dibenzoyl-4-phenyl-1, 2-dithiolane (*2a*) and 3,5-dibenzoyl-4-(4-tolyl)-1, 2-dithiolane (*2b*) were prepared by a one-pot reaction of thiocyanatoacetophenone (*1*) with the corresponding aromatic aldehydes in ethanol containing triethylamine at room temperature. The 3, 5-dibenzoyl-4-aryl-1, 2-dithiolanes (*2*) were converted into respective 2, 4-dibenzoyl-3,5-diarylthiolanes (*3*) by treatment with sodium ethoxide／ethanol.

The thiocyanato group which is often referred to as "Pseudohalogen", is strongrly electron-attractive. Therefore. it would be expected that thiocyanatoacetophenone (*1*) have an active methylene group. Accordingly, thiocyanatoacetophenone is structurally similar to halogenoacetophenones and cyanoacetophenone which easily react with the carbonyl compounds so far. This might be ascribed the fact that the thiocyanato group is extermely sensitive to the bases usually used as catalysis. giving cyclization compounds[1] or resinous matters.

However, if any suitable catalysis will be found, thiocyanatoacetophenone is to be expected to react with the aldehydes. The purpose of this series is to explore new possibility of as an active methylene compound.

In previous papers[2-5] on the reaction of thiocyanatoacetic ester with aldehydes, it was found that the base as catalyst might have some distinct effect on nature of the reaction. For the confirmation the authors have investigated the effects of triethylamine on the reaction of thiocyanatoacetophenone with aromatic aldehydes.

The reaction of thiocyanatoacetophenone with aromatic aldehydes was carried out in ethanol containing triethylamine. direct synthesis of 1, 3-oxathiolane derivatives being expected. However. an unexpected yellow crystalline product. 3, 5-dibenzoyl-4-aryl-1, 2-di-thiolanes (*2*), was obtained upon the treatment of thiocyanatoacetophenone with benzaldehyde or p-methylbenzaldehyde in ethanol containing triethylamine. The expected 1, 3-oxathiolane derivatives could not be isolated. On the other hand, the reaction of thiocyanatoacetophenone with other aromatic aldehydes in the presence of triethylamine under the same conditions afforded resinous matters.

The structure of 3, 5-dibenzoyl-4-aryl-4-1, 2-dithiolanes (*2*) was inferred from the results of microanalysis. I.R.. H-N.M.R. and M. S. spectra. The elemental analyses of *2a* (R＝H) indicated the composition as $C_{23}H_{18}O_2S_2$. As can be seen from experimental section,

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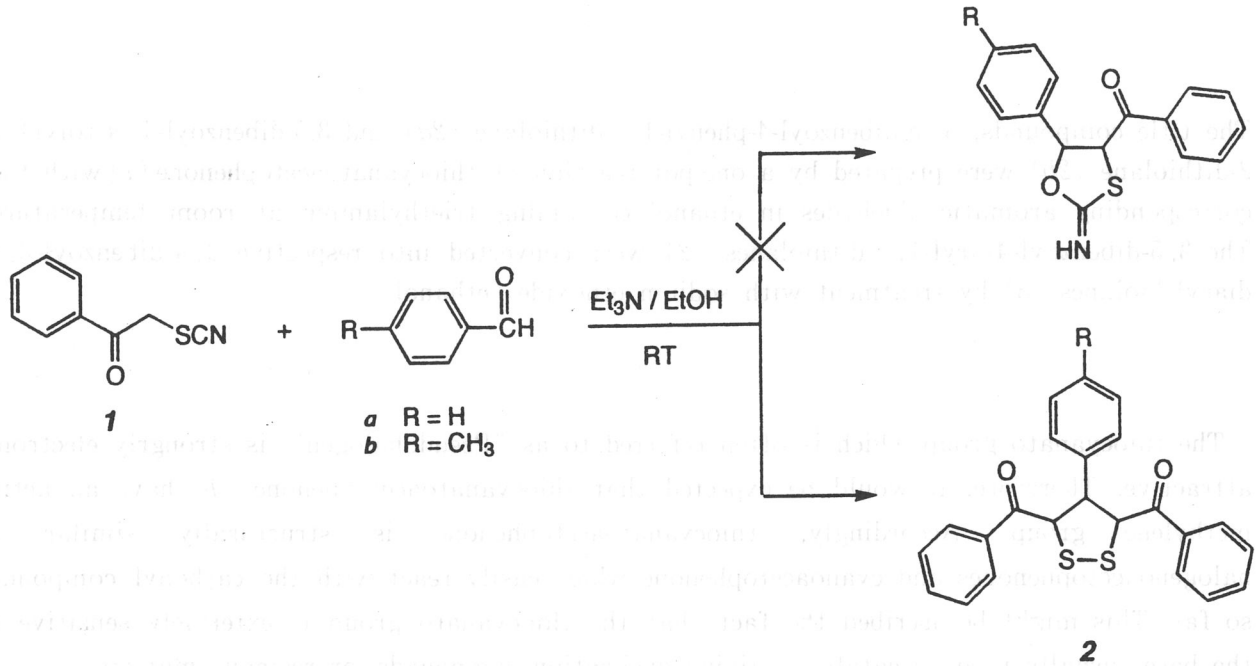
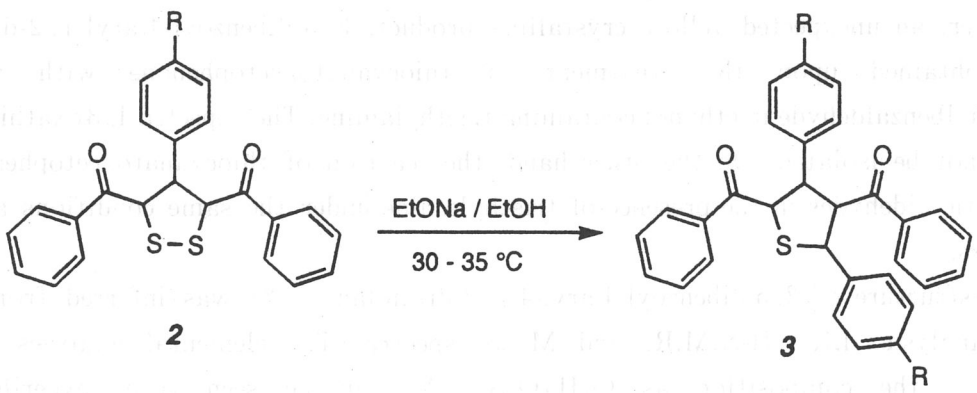
the H-N.M.R. spectrum of *2a* showed a sharp doublet signal(2H), the ^{3}C-H proton and ^{5}C-H proton on the dithiolane ring. and a sharp triplet signal(1H) of the ^{4}C-H proton on the dithiolane ring. The I.R. spectrunn of *2a* showed the presence of a typical ketone carbonyl group.



The procedure was applied in the synthesis of 3, 5-dibenzoyl-4-phenyl-1, 2-dithiolane(*2a* : mp 174-175℃) and 3,5-dibenzoyl-4-(4-tolyl)-1,2-dithiolane(*2b* : mp 183-183℃). Both *2a* and *2b* were converted into respective 2,4-dibenzoyl-3,5-diarylthiolanes (*3*) using common reduction by sodium ethoxide／ethanol.



For the comparison with 3, 5-dibenzoyl-4-aryl-1, 2-dithiolanes (*2*). the preparation of an authentic sample from diphenacyl disulphide[6] and benzaldehyde or p-methylbenzaldehyde was attempted under a variety of conditions, but 3, 5-dibenzoyl-4-aryl-1, 2-dithiolanes (*2*) could not be afforded from these reaction. This fact support the following pathway.

Pathway to *2*

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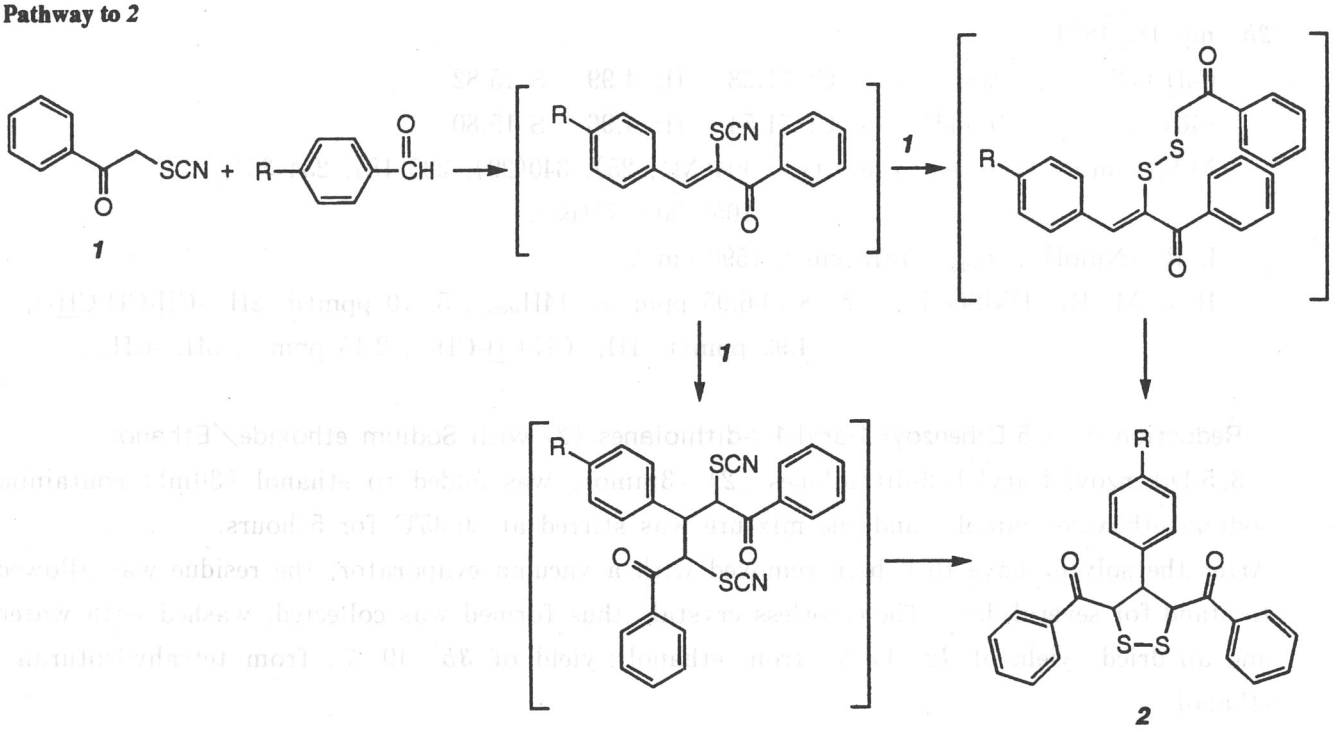

Experimental

All the melting points were taken on Mitamura Riken Kogyo melting point apparatus model 7-15 and are uncorrected. Microanalysis were measured with a Yanagimoto C. H. N. Corder MT-2 instrument. The I.R. spectra were obtained with a Hitachi 260-30 type spectrophotometer. The H-N.M.R. spectra were recorded on a Hitachi R-900 N.M.R. spectrometer at 90 MHz. using tetrametylsilane as the internal standard. Mass spectra were measured with a Hitachi M-52 GC-MS instrument operating at 70 eV.

Preparation of 3. 5-Dibenzoyl-4-aryl-1. 2-dithiolanes (*2*)

A mixture of thiocyanatoacetophenone (*1*) (10mmol) and benzaldehyde or p-methylbenzaldehyde (5mmol) in ethanol (5ml) containing thriethylamine (5mmol) was stirred at room temperature for 2 hours. The yellow crystals which precipitated out during the reaction were collected and washed with ethanol and ether. Recrystallization from tetrahydrofuran／ethanol gave 1, 2-dithiolane derivatives *2* ; yield of *2a* : 30 %, yield of *2b* : 27 %.

2a ; mp 174-175℃

$C_{23}H_{18}O_2S_2$ calc. (%) C: 70.76 H: 4.65 S 16.15

(390. 4) found(%) C: 70.54 H: 4.60 S 16.20

M.S. ; m/e (relative intensity) : 390(M^+, 18), 221(20), 220(59), 207(21), 105(100), 77(87).

I. R. (Nujol) ; ν_{max} : 1685 cm^{-1}, 1595 cm^{-1}.

H-N. M. R. (DMSO-d_6) ; δ: 8.10-7. 10 ppm(m, $15H_{arom}$), 5. 71 ppm(d, 2H, -CH-CH-CH-), 4.94 ppm(t, 1H, -CH-CH-CH-).

2b ; mp 182-183℃

$C_{24}H_{20}O_2S_2$ calc. (%) C: 71.28 H: 4.99 S 15.82

(404. 4) found(%) C: 71.54 H: 4.96 S 15.80

M.S. ; m/e (relative intensity) : 404(M^+, 25), 340(29), 235(18), 234(35), 105(100), 77(65).

I. R. (Nujol) ; ν_{max} : 1675 cm^{-1}, 1590 cm^{-1}.

H-N. M. R. (DMSO-d_6) ; δ: 8.10-6.95 ppm(m, $14H_{arom}$), 5. 70 ppm(d, 2H, -CH-CH-CH-), 4.92 ppm(t, 1H, -CH-CH-CH-), 2.15 ppm(s. 3H. $-CH_3$).

Reduction of 3. 5-Dibenzoyl-4-aryl-1.2-dithiolanes (*2*) with Sodium ethoxide/Ethanol

3, 5-Dibenzoyl-4-aryl-1, 2-dithiolanes (*2*) (3mmol) was added to ethanol (30ml) containing sodium ethoxide(5mmol), and the mixture was stirred at 30-35℃ for 5 hours.

After the solvent have then been removed with a vacuum evaporator, the residue was allowed to stand for several days. The colorless crystals thus formed was collected, washed with water, and air-dried ; yield of ***3a*** : 44 %, from ethanol ; yield of ***3b*** : 40 %, from tetrahydrofuran/ethanol.

3a ; mp 208-209℃

$C_{30}H_{24}O_2S$ calc. (%) C: 80.33 H: 5.39 S 7.13

(448. 5) found(%) C: 79.99 H: 5.46 S 7.08

M.S. ; m/e (relative intensity) : 448(M^+, 13), 240(24), 239(36), 209(38), 105(100), 77(43).

I. R. (Nujol) ; ν_{max} : 1675 cm^{-1}, 1660 cm^{-1}, 1595 cm^{-1}.

H-N. M. R. (DMSO-d_6) ; δ: 8.10-6.80ppm(m, $20H_{arom}$), 5.73ppm(d, 1H, $-^2CH-^3CH-^4CH-^5CH-$), 5.14ppm(t, 1H, $-^2CH-^3CH-^4CH-^5CH-$), 4.92ppm(d, 1H, $-^2CH-^3CH-^4CH-^5CH-$), 4.48ppnl(t, 1H, $-^2CH-^3CH-^4CH-^5CH-$).

3b ; mp 223-224℃

$C_{32}H_{28}O_2S$ calc. (%) C : 80.64 H : 5.92 S 6.71

(476. 5) found(%) C : 80.01 H: 6.01 S 6.68

M.S. ; m/e (relative intensity) : 476(M^+, 4), 371(3), 253(22), 223(30), 105(100), 77(26).

I. R. (Nujol) ; ν_{max} : 1685 cm^{-1}, 1665 cm^{-1}, 1600 cm^{-1}.

H-N. M. R. (DMSO-d_6) ; δ: 8.05-6.50ppm(m. $18H_{arom}$), 5.64ppm(d. 1H. $-^2CH-^3CH-^4CH-^5CH-$), 5.13ppm(t. 1H. $-^2CH-^3CH-^4CH-^5CH-$). 4.88ppm(d. 1H. $-^2CH-^3CH-$

^{4}CH-^{5}C<u>H</u>-), 4.43ppm(t, 1H. -^{2}CH-^{3}C<u>H</u>-^{4}CH-^{5}CH-),
2.22ppm(s, 3H, -CH_3), 2.13ppm(s. 3H. -CH_3).

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(Received Sept. 30, 1998)