# Reactions of Stable Ylidic 1-Thianaphthalene with Electrophiles.[1]
## A New Ring Expansion Reaction

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Reactions of 2-cyano-1-methyl-4-phenyl-1-thianaphthalene (1) with electrophiles, such as tetracyanoethylene, maleic anhydride, and 4-phenyl-1-thianaphthylium perchlorate gave the dimeric compound (II) of 1, but not any cycloaddition products. However, the treatment of 1 and dimethyl acetylenedicarboxylate afforded a new ring expansion product (III) having sulphur-containing nine-membered ring.

Recently, much attention has been focussed on thiabenzenes in organic chemistry.[2a,3a] Some stable ylidic 1,2-disubstituted 2-thianaphthalenes,[2b,3b] and 9,10-disubstituted 10-thiaanthracenes[2c,2d] have been reported. However, report on the title ring system has not been done.

In this communication, we wish to describe the reactions of a typical 1-thianaphthalene derivative (I)[1] with electrophiles, such as tetracyanoethylene (TCNE), maleic anhydride, 4-phenyl-1-thianaphthylium perchlorate, and dimethyl acetylenedicarboxylate (DMAD). And also, especially, discussion will be made on a new ring expansion reaction using I with DMAD.

Stirring I with TCNE in benzene at room temperature under nitrogen stream for 12 hr gave dimeric compound (II) of I in 9.3 % yield, the recovered TCNE and black resins of undetermined structure. The physical data of II are as follows : m.p. 279-281° ($C_{34}H_{26}N_2S_2$) as orange needles (benzene-pet.ether) : mass (m/e) : 526 ($M^+$) : ir (KBr) $\nu$ max $cm^{-1}$ ; 2225 (CN) ; nmr ($C_6D_6$) ; $\delta$ 1.90 (3H, s, S-$CH_3$), 6.85-7.50 (10H, m, olefinic and aromatic H). Similarly, II was also obtained by the treatment of I with maleic anhydride in benzene for 30 hr in 10 % yield and with 4-phenyl-1-thianaphthylium perchlorate in $CH_2Cl_2$ for 6 hr in 30 % yield besides the recovered 4-phenyl-1-thianaphthylium perchlorate in 77.3 %, but any isolable cycloaddition products were not obtained.

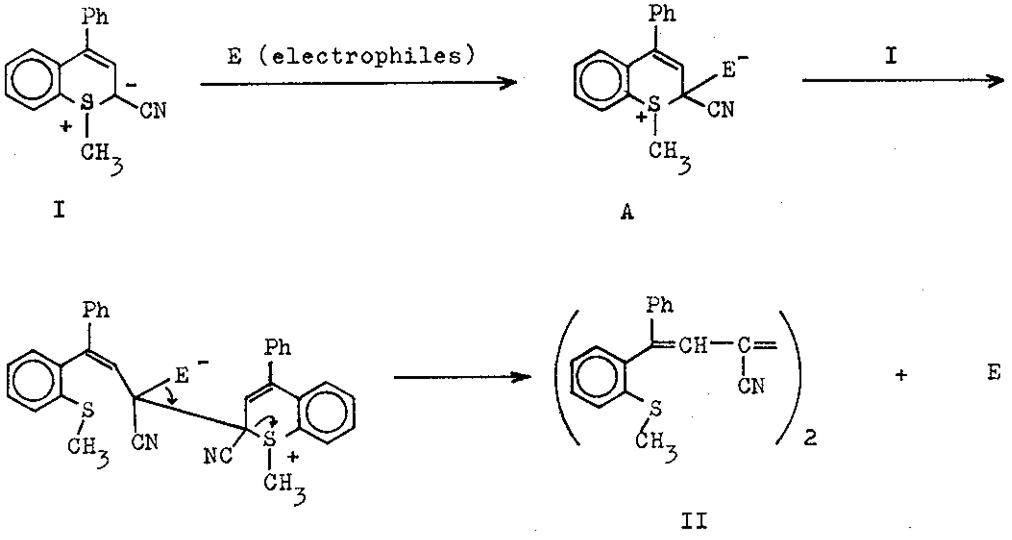
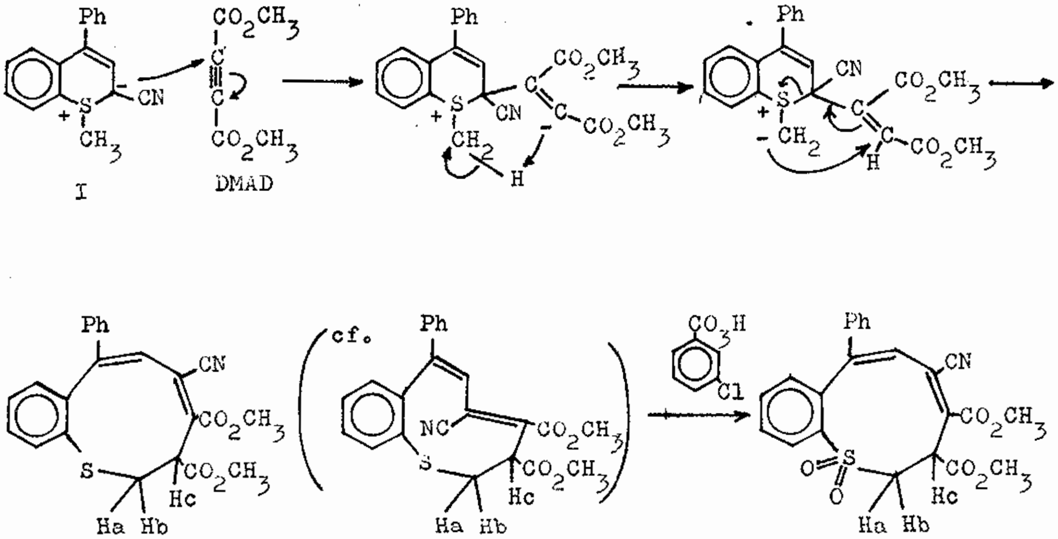


Chart 1

From the above data, the authors propose the mechanism for the reaction of I with these electrophiles as shown in Chart 1.

On the other hand, the treatment of I with 2 eq DMAD in a manner similar to the case of TCNE, yielded an interesting ring expansion product (III) : m.p. 142-149° ($C_{23}H_{19}O_4NS$) as colorless prisms (ether) : mass (m/e) 405 ($M^+$) : ir (KBr) $\nu$ max $cm^{-1}$ ; 2220 (CN), 1740 and 1710 (CO) : nmr ($CDCl_3$) $\delta$ 2.98 (1H, d,d, $J_{ab}$ = 15 Hz, $J_{ac}$= 9 Hz, $H_a$), 3.68 (3H, s, $CO_2CH_3$), 3.71 (1H, broad d, $J_{ab}$ = 15 Hz, $J_{bc}$ = 0 Hz, $H_b$), 3.72 (3H, s, $CO_2CH_3$), 4.20 (1H, broad d, $J_{ac}$ = 9 Hz, $J_{bc}$ = 0 Hz, $H_c$), 6.90 (1H, s, olefinic H), and 7.20-8.00 (9H, m, aromatic H). Subsequently, III was successively oxidized with m-chloroperbenzoic acid in $CH_2Cl_2$ over night at 0° to give sulfone derivative (IV) in 77.8 % yield : m.p. 192-193° ($C_{23}H_{19}O_6NS$) as colorless prisms (ether) : ir (KBr) $\nu$ max $cm^{-1}$ ; 2225 (CN), 1740 (CO), 1318 and 1058 ($SO_2$) : nmr ($CDCl_3$) $\delta$ 3.45 (1H, d,d, $J_{ab}$ = 17 Hz, $J_{ac}$ = 10 Hz, $H_a$), 3.78 (6H, s, $CO_2CH_3$), 4.28 (1H, broad d, $J_{ab}$ = 17 Hz, $J_{bc}$ = 0 Hz, $H_b$), 4.50 (1H, broad d, $J_{ac}$ = 10 Hz, $J_{bc}$= 0 Hz, $H_c$), 6.83 (1H, s, olefinic H), 7.30-8.30 (9H, m, aromatic H). However, it is difficult to determine the stereochemical assignments of cis and trans isomers of III. Quite recently, Vedejs et al.[4] reported on synthesis of eight-membered ring compound having a cis double bond as major product starting from sulphur ylide containing five-membered ring. Thus, III can be assigned to the cis form by the stereochemical requirement on the transition state.

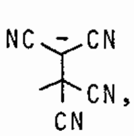
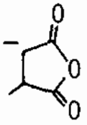
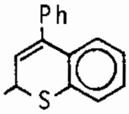
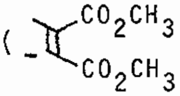
The formation of III is presumed to proceed through the five-centered transition state as shown in Chart 2.



I DMAD

III : cis form III : trans form IV

Chart 2

Finally, concerning with the intermediate A in Chart 1 : When E$^-$ ( ,  and  ) is rather stable, the reaction might proceed to give the dimeric product. When E$^-$ (  ) is more basic than the above described species, the intramolecular deprotonation might occur to give the authors' intermediate ylide in Chart 2.

Further related studies directed toward the applications to synthetic and theoretical organic chemistry are also in progress.

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