HETEROCYCLES, Vol. 7, No. 2, 1977

REACTIONS OF NEW CYCLIC SULPHUR 1,4-YLIDE, 9-CYANO-10-METHYL-10-THIAANTHRACENE WITH ELECTROPHILES.[1]

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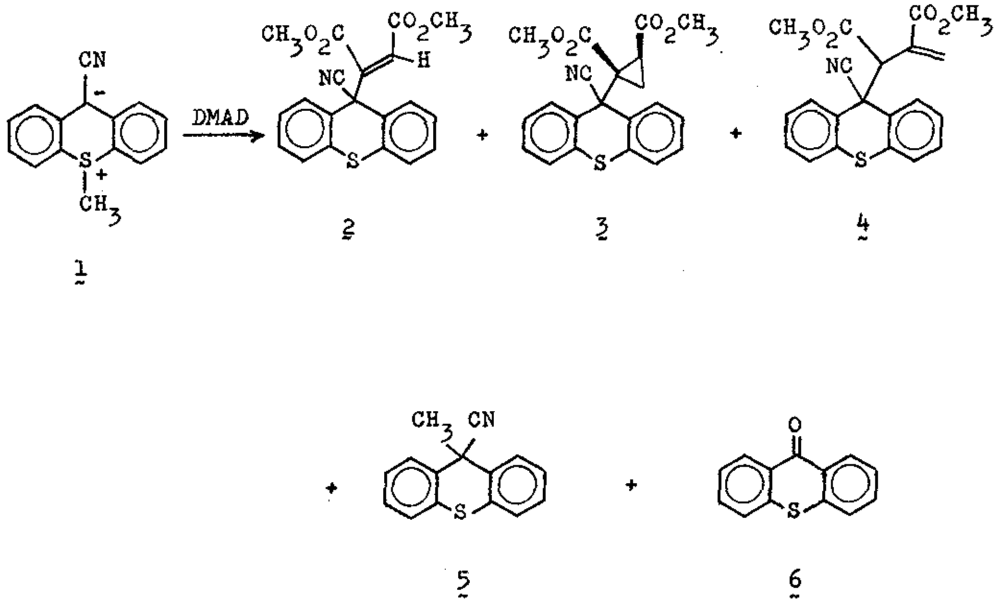
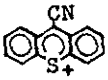
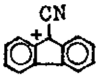
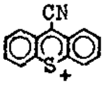
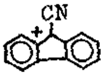
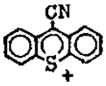
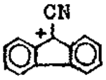
Reaction of 9-cyano-10-methyl-10-thiaanthracene (1) and dimethyl acetylenedicarboxylate gave the novel intramolecular rearrangement products, 9-cyano-9-R-thioxanthenes (2, 3, and 4) besides 9-cyano-9-methylthioxanthene (5) and thioxanthone (6). And also 9-cyano-9-(dicyanomethyl)thioxanthene (12) and others were obtained from the treatment of 1 with tetracyanoethylene.

Although much attention has been directed toward the chemistry of thiabenzenes,[2-4] report on the stable thiaanthracene derivatives has not been described. In this communication, we wish to report the reactions of a new crystalline cyclic sulphur 1,4-ylide, 9-cyano-10-methyl-10-thiaanthracene (1)[1a] with electrophiles, such as dimethyl acetylenedicarboxylate (DMAD) and tetracyanoethylene (TCNE).

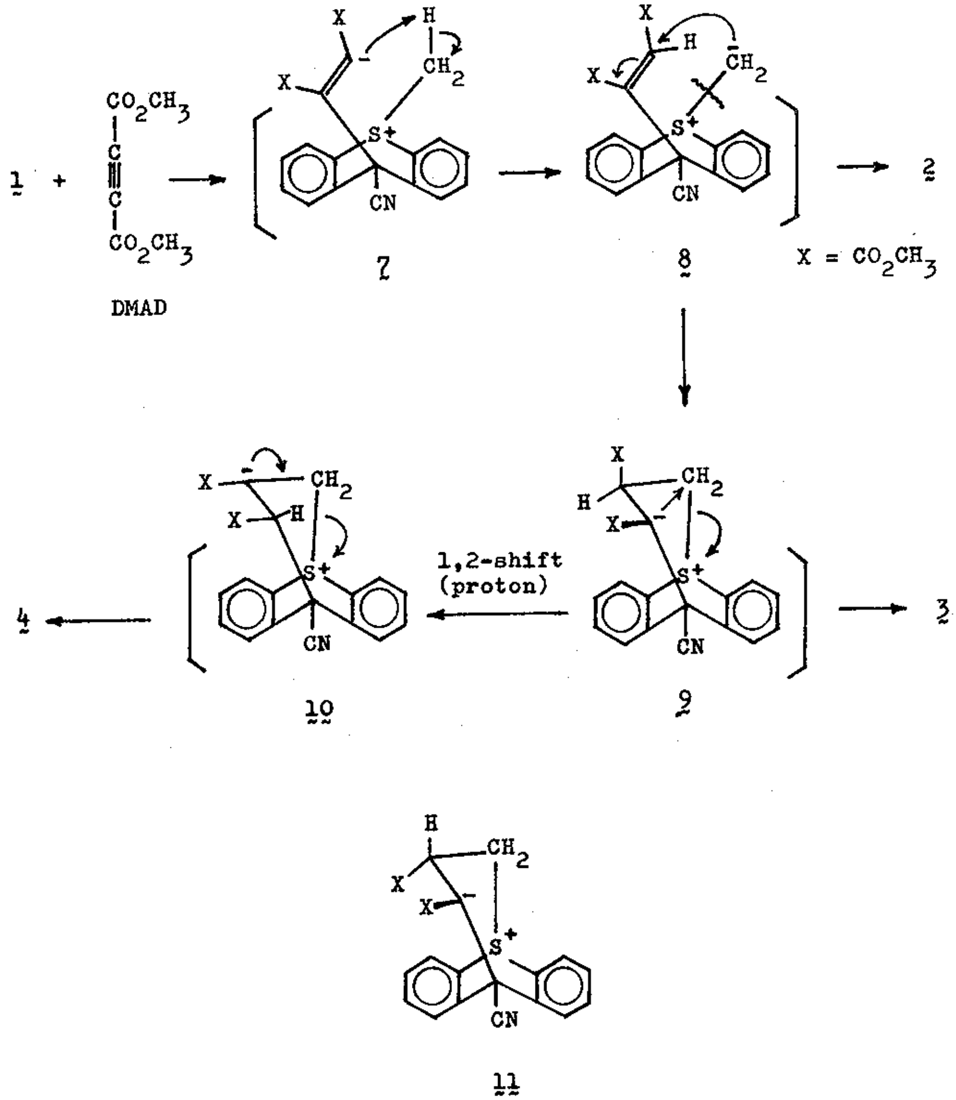
A solution of 1 (680 mg) and DMAD (450 mg) in benzene (20 ml) was stirred at room temperature under nitrogen stream for 40 hr.

Evaporation of the solvent and then the reaction mixture was purified by the preparative thin-layer chromatography on silica-gel (CH_2Cl_2) to isolate dimethyl 9-cyanothioxanthen-9-ylmaleate (**2**), dimethyl *1-(9-cyanothioxanthen-9-yl)cyclopropane-cis-1,2-*dicarboxylate (**3**), dimethyl 1-(9-cyanothioxanthen-9-yl)-2-propene-1,2-dicarboxylate (**4**), 9-cyano-9-methylthioxanthene (**5**), and thioxanthone (**6**)[5] in yields of 288 mg (28 %), 45 mg (4 %), 95 mg (9 %), 120 mg (18 %), and 55 mg (9 %), respectively. The physical data of **2** : mp 149-151° ($C_{20}H_{15}NO_4S$) as colorless



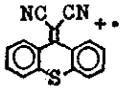
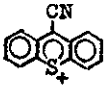
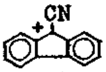
needles (CH_2Cl_2-pet. ether) : nmr ($CDCl_3$) δ 3.48 (3H, s, OCH_3), 3.63 (3H, s, OCH_3), 5.30 (1H, s, =CH), 7.25-7.66 (6H, m, Ar_{2-7}-H), 7.80-8.12 (2H, m, $Ar_{1\text{ and }8}$-H) : ir (KBr) ν max cm^{-1} ; 2260 (CN), 1727 (CO_2), 1633 (C=C) : mass (m/e, $I^{\%}$ rel.) 366 (M^++1, 3), 365 (M^+, 13), 222 ( , 100), 190 ( , 10), and so on. ; 3 : mp 183-184° ($C_{21}H_{17}NO_4S$) as colorless plates (CH_2Cl_2-ether) : nmr ($CDCl_3$) δ 0.57-0.99 (1H, m, cyclopropane), 1.57-1.95 (2H, m, cyclopropane), 3.39 (3H, s, OCH_3), 3.67 (3H, s, OCH_3), 7.20-7.63 (6H, m, Ar_{2-7}-H), 7.75-8.08 (2H, m, $Ar_{1\text{ and }8}$-H) : ir (KBr) ν max cm^{-1} ; 2260 (CN), 1746 and 1728 (CO_2) : mass (m/e, $I^{\%}$rel.) 379 (M^+, 1), 222 ( , 100), 190 ( , 19), and so on. ; 4 : mp 112-114° ($C_{21}H_{17}NO_4S$) as colorless prisms (ether-pet. ether) : nmr ($CDCl_3$) δ 3.33 (3H, s, OCH_3), 3.39 (3H, s, OCH_3), 5.06 (1H, s, $CHCO_2$), 6.57 (2H, s, =CH_2), 7.09-7.78 (7H, m, Ar_{1-7}-H), and 7.90-8.18 (1H, m, Ar_8-H) : (DMSO-d_6) δ 3.28 (3H, s, OCH_3), 3.36 (3H, s, OCH_3), 4.94 (1H, s, $CHCO_2$), 6.40, 6.49 (2H, s, =CH_2), and 7.27-8.00 (8H, m, ArH) : ir (KBr) ν max cm^{-1}; 2260 (CN), 1735 and 1721 (CO_2), 1618 (C=C) : mass (m/e, $I^{\%}$rel.) 379 (M^+, 0.5), 222( , 100), 190 ( , 19), and so on. ; 5 : mp 68-69° ($C_{15}H_{11}NS$) as colorless prisms (ethanol) : nmr ($CDCl_3$) δ 1.78 (3H, s, CH_3), 7.19-7.60 (6H, m, Ar_{2-7}-H), and 7.78-8.11 (2H, m, $Ar_{1\text{ and }8}$-H) : ir (KBr) ν max cm^{-1} ; 2250 (CN).

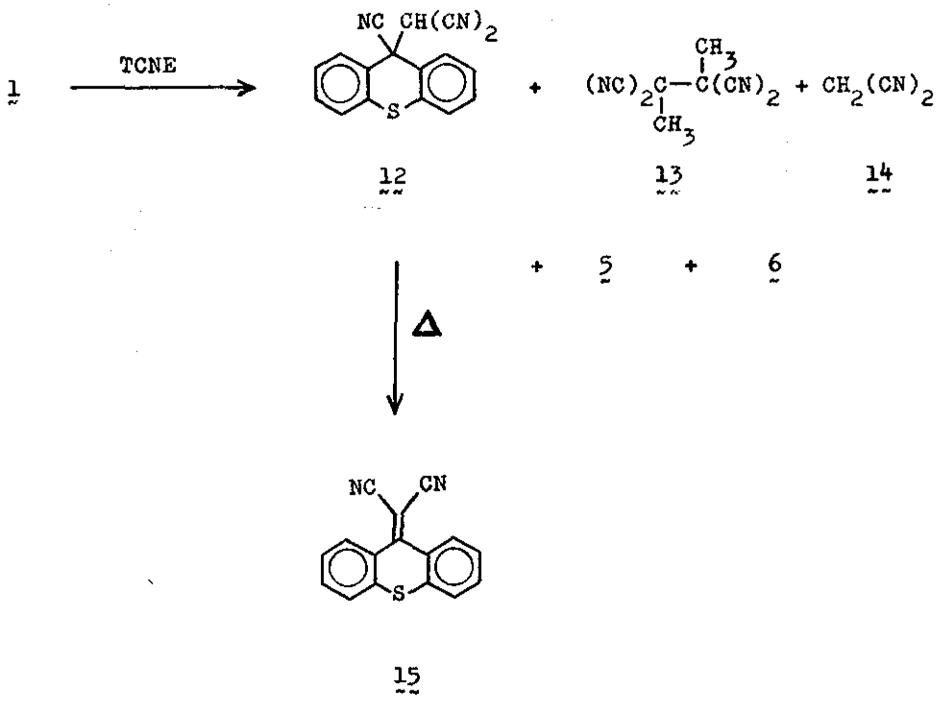
From the above data, the formation of 2, 3, and 4 is considered to proceed as shown in Scheme I. The initial step of the reaction gives undoubtedly the first intermediate (7) which then abstracts a proton of S-methyl group intramolecularily to form the second intermediate, methylide (8) from which the elimination of methylene group would yield 2.



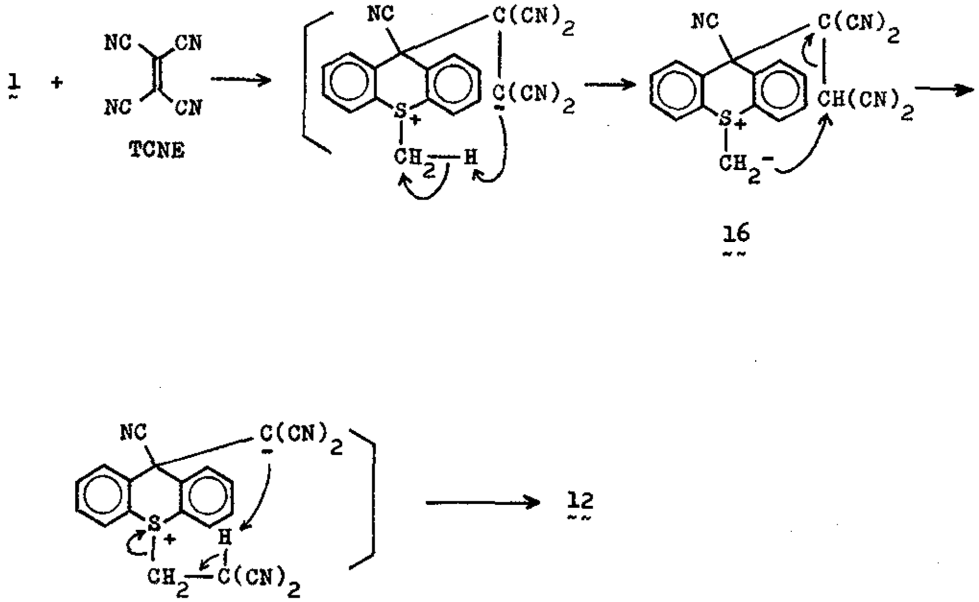
Scheme I.

Furthermore, the anionic site of 8 attacks the double bond to form the third intermediate (9) which gives intramolecularily 3 via S_N-reaction for the sulphonium group and also 4 via Elcb-reaction in the fourth intermediate (10). Intermediate, 11 will be less preferable than 9 by the stereochemical requirement. Finally, the formation of 5 or 6 can be explained by the Stevens-type 1,4-sigmatropic rearrangement[2b, 3b] or the autoxidation of 1.

On the other hand, the treatment of 1 (820 mg) in THF (10 ml) with TCNE (500 mg) at room temperature under nitrogen stream for 24 hr yielded 9-cyano-9-(dicyanomethyl)thioxanthene (12), 2,2,3,3-tetracyanobutane (13), and malononitrile (14)[6] with the formation of 5 and 6[5] in yields of 105 mg (11 %), 130 mg (24 %), 120 mg (47 % from TCNE), 70 mg (8.5 %), and 95 mg (13 %), respectively by means of column chromatography on silica-gel ($CHCl_3$). The physical data of 12 : mp>130° (decomp.), ($C_{20}H_9N_5S$) as colorless needles (CH_2Cl_2-cyclohexane) : nmr ($CDCl_3$) δ 4.98 (1H, s, CH), 7.45-7.81 (6H, m, Ar_{2-7}-H), 8.00-8.32 (2H, m, Ar_{1} and $_{8}$-H) : ir (KBr) ν max cm^{-1} ; 2890 (CH), 2260 (CN) : mass (m/e, $I^{\%}$rel.) 287 (M^+, 1), 260 ( , 58), 222 ( , 100), 190 ( , 17), and so on. ; 13 : mp 190-192° (in sealed tube), ($C_8H_6N_4$) as colorless plates (CH_2Cl_2-$CHCl_3$) : nmr (DMSO-d_6) δ 2.23 (6H, s, CH_3x2) ; 14 : bp 109° (20 mmHg), (in microdistillation) : nmr ($CDCl_3$) δ 3.65 (2H, s, CH_2) : ir (neat) ν max cm^{-1} ; 2280 (CN). The compound, 12 (25 mg) was also chemically confirmed by heating at 150° for 3 hr to afford 9-dicyanomethylenethioxanthene (**15**), mp 300-303° as yellow fine needles (CH_2Cl_2) in yield of 19 mg (80 %) which was identified by the melting point test and from the comparison of ir and uv spectral data with those of an authentic sample.[7]



Thus, these results seem to suggest that the formation of **12** proceeds also intramolecularily via the second intermediate, methylide (**16**) as shown in Scheme II.



Scheme II.

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Received, 5th August, 1977