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SYNTHESIS AND PROPERTIES OF THE FIRST CRYSTALLINE 1,4-YLIDE, 9-CYANO-10-METHYL-10-THIAANTHRACENE[1]

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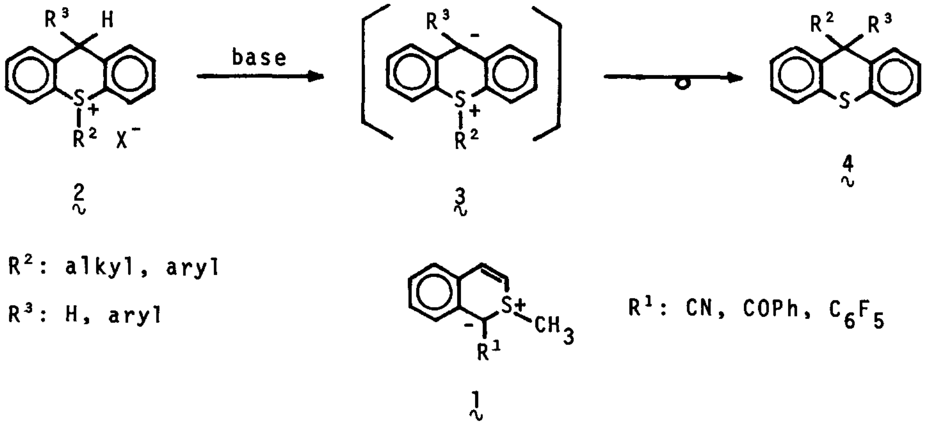
Recently, much interest has been focussed on the chemistry of thiabenzenes, in particular, the preparation and properties of the stable thiabenzene derivatives. 1-Cyano-,[1,2] benzoyl-,[1,2] and pentafluorophenyl-2-methyl-2-thianaphthalenes[3] (**1**) having electron-attracting groups at 1-position, were isolated as stable compounds. However, cyclic sulfur 1,4-ylides, namely, 9,10-disubstituted 10-thiaanthracenes (**3**) formed by the treatment of 9,10-disubstituted thioxanthenium salts (**2**) with bases are quite unstable compounds which undergo thermal Stevens-type 1,4-rearrangement reaction to yield the corresponding 9,9-disubstituted thioxanthenes (**4**).[1,3,4] Hence, no report has been described on the stable thiaanthracene derivatives so far.

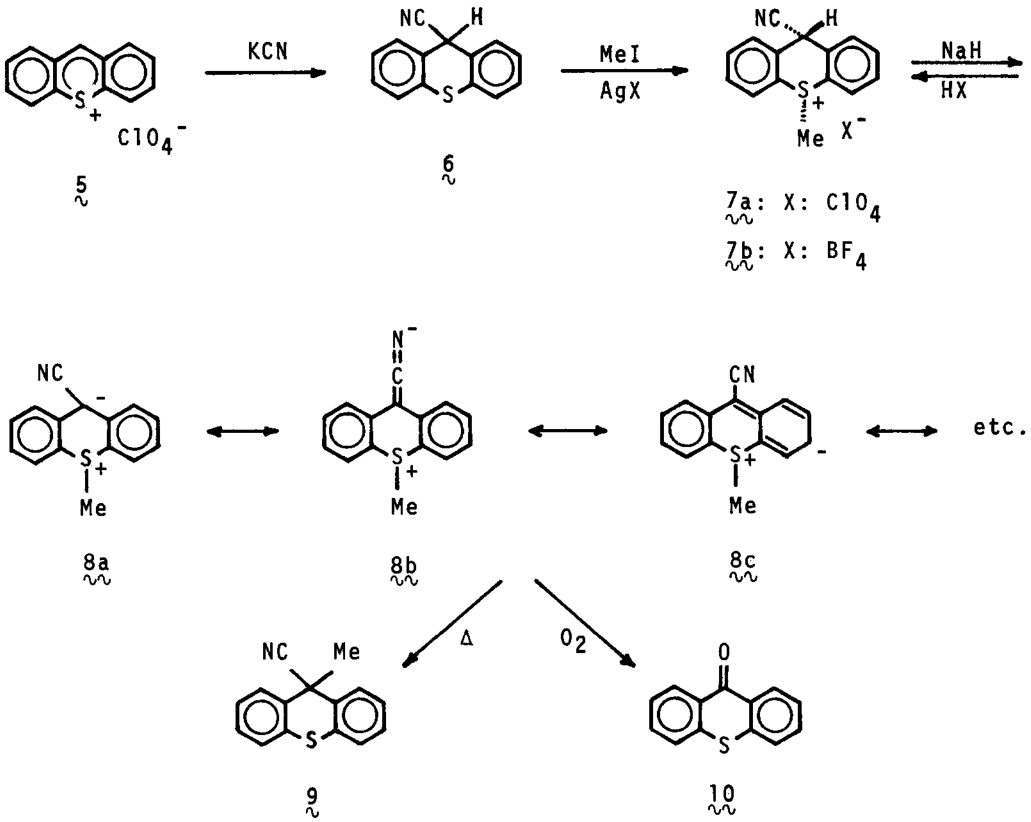


Scheme I

In this communication, we wish to report the first synthesis of a crystalline cyclic sulfur 1,4-ylide, 9-cyano-10-methyl-10-thiaanthracene (**8**) by the reaction of 9-cyano-10-methylthioxanthenium salts (**7**) with NaH.[1,5]

Treatment of thioxanthylium perchlorate (**5**)[6] with KCN in H_2O-CH_2Cl_2 afforded 9-cyanothioxanthene (**6**),[7] in 95 % yield, which was methylated with MeI in the presence of $AgClO_4$ or $AgBF_4$ to give 9-cyano-10-methylthioxanthenium perchlorate (**7a**)[8] with colorless prisms (from acetone), mp 181-183° (decomp.) in 54 % yield: NMR (CF_3CO_2H) δ 3.48 (3H, s, Me), 6.25 (1H, s, C_9-H), and 7.73-8.46 (8H, m, ArH); IR (KBr) ν max cm^{-1} 2240 (CN) and 1147-1082 (ClO_4^-), and tetrafluoroborate (**7b**)[8] with colorless scales (from acetone-ether), mp 186-189° (decomp.) in 64 % yield: NMR (CF_3CO_2H) δ 3.46 (3H, s, Me), 6.22 (1H, br. s, C_9-H), and 7.76-8.49 (8H, m, ArH); IR (KBr) ν max cm^{-1} 2240 (CN) and 1062-1033 (BF_4^-), respectively. Deprotonation of both **7a** and **7b** using NaH in THF under nitrogen atmosphere yielded 9-cyano-10-methyl-10-thiaanthracene (**8**), which is the first example of a stable and crystalline 1,4-ylide in thiaanthracene system, with orange-yellow needles (from CH_2Cl_2-ether), mp 115-116° in 94 % yield: NMR ($CDCl_3$) δ 2.22 (3H, s, Me), 6.73-7.06 (2H, m, $C_{3\text{ and }6}$-H), and 7.19-7.77 (6H, m, ArH); IR (KBr) ν max cm^{-1} 2170 (CN); Field Desorption(FD) MS (m/e) 237 (M^+) which is supported as monomeric. The absorption band of cyano group in the IR spectrum of **8** is stronger and shifts to lower wave number compared with that of ordinary cyano group, indicating the delocalization of the carbanion electron of **8** through the cyano group.

Thiaanthracene (**8**) was acidified with $HClO_4$ or HBF_4 to afford the starting thioxanthenium salt (**7a**) or (**7b**), respectively. On standing in THF at 50° for 5 hr under nitrogen atmosphere, **8** gave thermal 1,4-rearrangement product, 9-cyano-9-methylthioxanthene (**9**)[11] with colorless prisms (from EtOH), mp 68-69° in 82 % yield: NMR ($CDCl_3$) δ 1.78 (3H, s, Me), 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), which was also synthesized by the reaction between 9-methylthioxanthylium perchlorate[6] and KCN-H_2O in CH_2Cl_2. When **8** was stirred in THF till it became colorless, thioxanthone (**10**) was afforded by the autoxidation as colorless needles (from benzene), mp 218-220°, (lit[9] mp 219°) in 88 % yield.



Scheme II

The very interesting reaction of 8 with some electrophiles will be also reported in the quite near future.10)

REFERENCES AND FOOTNOTES

1) A part of this work was presented at a) the 5th International Congress of Heterocyclic Chemistry, Ljubliana, Yugoslavia, July, 1975, Abstracts of Papers p. 299; b) the 8th Congress of Heterocyclic Chemistry, Kyoto, Japan, Oct., 1975, Abstracts of Papers p. 119 by M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, and H. Aoki.

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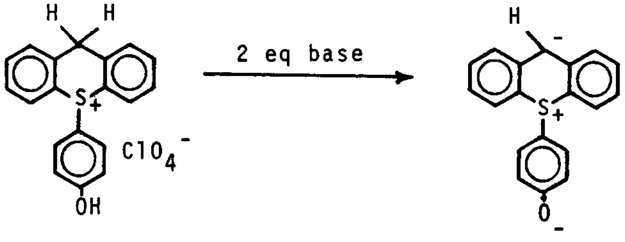
3) a) B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **97**, 2718 (1975); b) J. Stackhouse, B. E. Maryanoff, G. H. Senkler, Jr., and K. Mislow, *ibid.*, **96**, 5650 (1974).

4) a) M. Hori, T. Katoka, and H. Shimizu, *Chemistry Letters*, 1117 (1974); b) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5648 (1974); c) F. Ogura, W. D. Hounshell, C. A. Maryanoff, W. J. Richter, and K. Mislow, *ibid.*, **98**, 3615 (1976); d) H. Pirelahi, Y. Abdoh, and A. Afzali, *Tetrahedron Letters*, 4609 (1976).

5) Mislow and his co-workers generated **12** with remarkable stability in solution, by the treatment of **11** with 2 eq of dimsylsodium in DMSO, but they could not isolate it.4c)



11 **12**

6) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

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8) In the Scheme II, dotted lines drawn in the figure of compound **7** indicate pseudo-equatorial bonds. Configuration of **7a** is cis form, and that of **7b** is cis form in the state of crystal, but in CF_3CO_2H solution, a part of cis form changes to trans form (cis/trans = 1.55). Trans **7b** : NMR (CF_3CO_2H) δ 3.67 (3H, s, Me) and 6.07 (1H, s, C_9-H).

9) M. Gomberg and W. Minnis, *J. Amer. Chem. Soc.*, **43**, 1940 (1921).

10) M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, *Heterocycles, Vol. 7*, special issue dedicated to Prof. R. B. Woodward on the occasion of his 60th birthday, in press.

11) Satisfactory analytical data were obtained for all new compounds.