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REINVESTIGATION OF THIABENZENES
A NEW RESULT OF THE REACTION OF 9-PHENYLTHIOXANTHYLIUM SALT AND PHENYLLITHIUM[1)]

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Summary "9,10-Diphenyl-10-thiaanthracene" was found to be a mixture of monomeric species such as 9-phenyl-, 9,9-diphenyl-, 3,9-diphenyl-, 3,9,9-triphenyl- and 4,9,9-triphenylthioxanthenes, and several kinds of dimers and so on Some of them were formed by radical phenylation The mechanism was proposed

Thiabenzenes have attracted the attention of many chemists[2)] since Price and Suld reported the synthesis of 1,2,4,6-tetraphenylthiabenzene from 2,4,6-triphenylthiopyrylium salt and phenyllithium.[3)] We also reported that the reaction of 10-aryl-9-phenylthioxanthenium salts with bases generated the ylidic intermediates and proceeded via Stevens type 1,4-sigmatropic rearrangement to give 9-aryl-9-phenylthioxanthenes.[4)] Descriptions were made on the synthesis and the reactions of crystalline ylidic 1-benzoyl(or cyano)-2-methyl-2-thianaphthalene[5)] and 9-cyano-10-methyl-10-thiaanthracene [6)] Very recently we succeeded in X-ray analysis of 1-benzoyl-2-methyl-2-thianaphthalene and the result will be published elsewhere On the other hand, Mislow and co-workers[7)] pointed out the contradiction between two kinds of methods for preparing thiabenzenes, namely, the reactions of thiopyrylium salts with phenyllithium[8)] and the deprotonation of sulfonium salts with strong bases [4,9)] From their experimental results, it was concluded that thiabenzenes were ylides and underwent thermal Stevens rearrangement to thiopyrans, and that the "stable thiabenzenes" from the reactions of thiopyrylium salts with phenyllithium were not monomeric compounds but oligomeric materials of which molecular weights were three to six times greater than expected for monomeric species

We have closely examined so-called "9,10-diphenyl-10-thiaanthracene", mp 146-148°(dec.) claimed by Price, et al [8)] in order to elucidate the structure for a long period In this communication, we would like to describe a new result on the reaction of 9-phenylthioxanthylium salt and phenyllithium which proceeded via a radical process besides Stevens rearrangement "9,10-Diphenyl-10-thiaanthracene" was synthesized by the same way as in the earlier paper[8)] and mass spectra were measured [10)] Peaks with m/e values greater than 350, which corresponds to the molecular weight of monomeric 9,10-diphenyl-10-thiaanthracene, appeared at m/e 360, 366, 426, 502, 546 and 622 (the last three peaks were very small) in the EI mass spectrum (70eV) (Fig Ia), and m/e 366, 382, 426, 442, 484, 502, 546, 562, 578, 622, 638, 654, 698, 714, 730, 756, 774, 818 and so on in the FD mass spectrum (18 mA) (Fig Ib) The striking difference between them indicates that molecular weights of thiabenzenes are impossible to measure by the EI spectrometry and the FD mass spectrometry should be used for the purpose The FD mass spectra definitely showed it consisted of several compounds

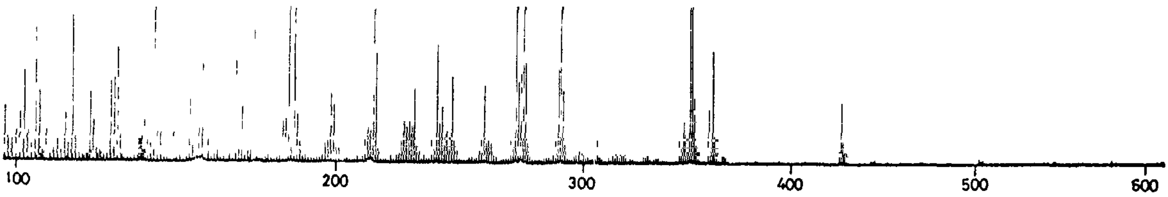

Fig Ia An EI mass spectrum of "9,10-diphenyl-10-thiaanthracene"

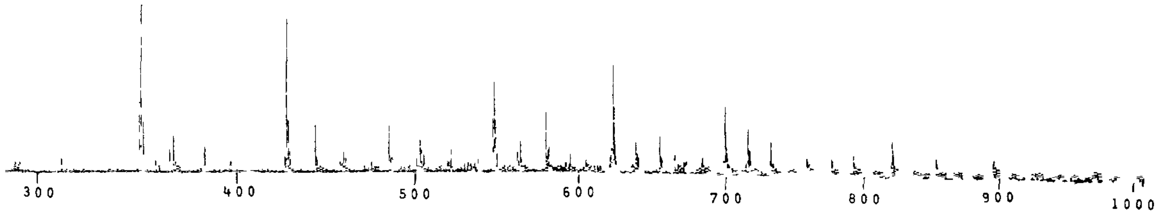

Fig Ib An FD mass spectrum of "9,10-diphenyl-10-thiaanthracene"

On the basis of these mass spectral data, we further separated "9,10-diphenyl-10-thiaanthracene" (650 mg) by means of column, thin layer (TLC) and high pressure liquid chromatography (HPLC) as follows The thiaanthracene was column-chromatographed on silica gel (Wakogel C-200) using benzene-hexane (Ratio was changed in the range of benzene/hexane = 0-10) and then ether Since some fractions from benzene-hexane eluates were still a mixture, they were separated by TLC on silica gel Compounds obtained were 9-phenylthioxanthene[8] (2, 25 mg), 9,9-diphenylthioxanthene[8,11] (3, 172 mg), 3,9-diphenylthioxanthene[12] (4, 43 mg), 3,9,9-triphenylthioxanthene[12] (5, 25 mg), 4,9,9-triphenylthioxanthene[12] (6, 95 mg), 9-phenylthioxanthyl dimer[11] (7, 8 mg), thioxanthone[11] (8, 10 mg), 9-phenylthioxanthyl peroxide[11] (9, 10 mg) and a mixture (A, 75 mg, colorless prisms from hexane, mp 260-262°) of compounds of which molecular weights were 546, 622 and 698 The mixture A was separated by HPLC on JASCOSIL SS-05 using hexane-CH_2Cl_2 (100 5), but structure of the constituents has not been determined yet A fraction from ether eluate gave a brown amorphous solid of which IR spectrum showed the presence of sulfoxides [(KBr) cm^{-1} 1040 (S-O)] The presence of sulfoxides in the "10-thiaanthracene" was predicted by the peaks at m/e 366, 442, 562 and so forth in the FD mass spectrum (Fig Ib) The solid from ether eluate was reduced with $LiAlH_4$ and then separated by TLC on silica gel using benzene-hexane to give 2 (15 mg), 3 (20 mg), 4 (10 mg) and a mixture (B, 15 mg, colorless prisms from EtOH, mp 157-159°) of compounds of which molecular weights were 622, 698 and 774 The mixture B was further separated

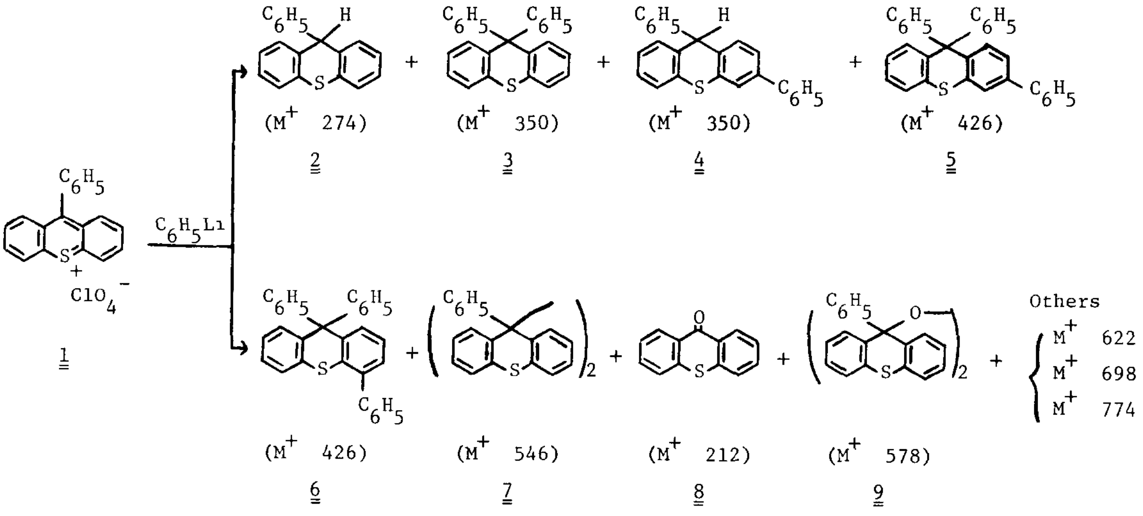

Chart 1

by HPLC using hexane-CH_2Cl_2 (10 1), but structure of the constituents has been undetermined. (see Chart 1)

Based on the above results,13) we propose the radical mechanism14) for the reaction as shown in Chart 2

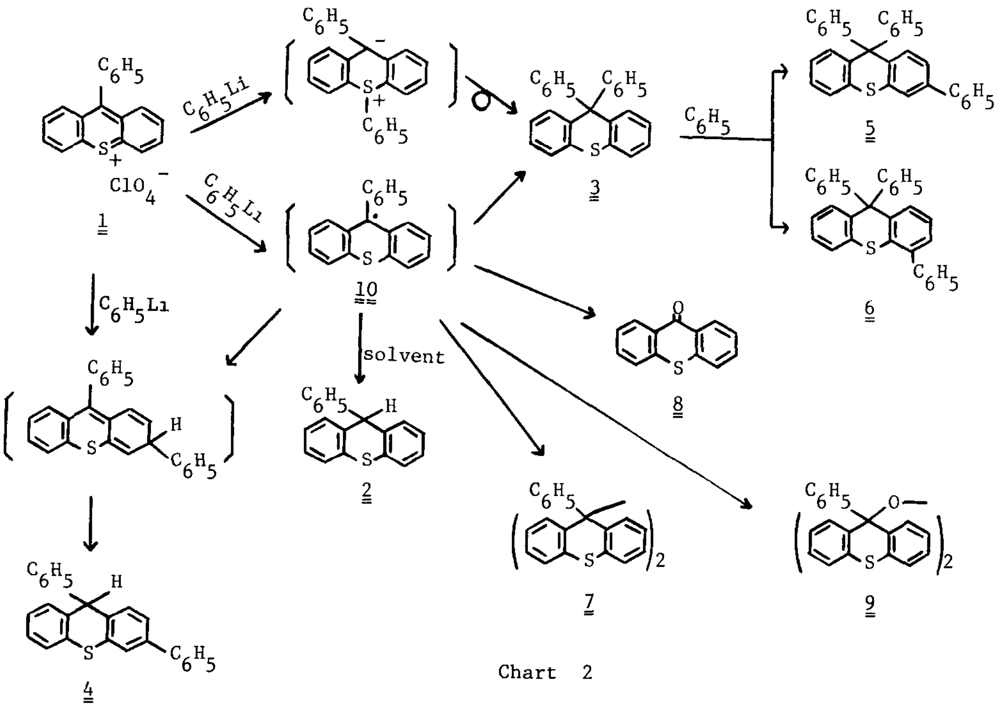

Chart 2

Further investigation of the compounds with molecular weights 622, 698 and 774[15] is in progress We concluded that "9,10-diphenyl-10-thiaanthracene" was a mixture of monomeric 9,9-diphenylthioxanthene, radical phenylated 9-phenylthioxanthenes, radical phenylated 9-phenylthioxanthene dimers and so forth It is assumed that "9,10-diphenyl-10-selenaanthracene" has the same features as "9,10-diphenyl-10-thiaanthracene "[16] However, "thianaphthalenes" are supposed to be the mixtures of oligomers because the C-S bond in the bicyclic ring system is easily cleaved[17] and complicated reactions may occur

REFERENCES AND FOOTNOTES

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9) M Hori, T Kataoka, H Shimizu, and C -F Hsu, Chem Lett , 391 (1973)
10) The EI and FD mass spectra were measured with a JEOL 01SG spectrometer at an ionizing voltage of 70 eV, and a JEOL JMS 01SG-2 double focussing spectrometer of which highest measurable mass number is 1500 at an emitter current of 15-18 mA, respectively
11) M Hori, T Kataoka, Y Asahi, and E Mizuta, Chem Pharm Bull (Tokyo), 21, 1692 (1973)
12) Physico-chemical data of new compounds isolated are 4, colorless prisms, mp 135° (hexane) Anal $C_{25}H_{18}S$ NMR ($CDCl_3$) δ 5 36 (1H, s, C_9-H), 7 0-7 85 (17H, m, ArH), 5, colorless prisms, mp 212° (benzene-hexane) Anal $C_{31}H_{22}S$ NMR ($CDCl_3$) δ 6 7-7 75 (m, ArH), 6, colorless prisms, mp 192° (benzene-hexane) Anal $C_{31}H_{22}S$ NMR ($CDCl_3$) δ 6 7-7 5 (17H, m, ArH), 7 38 (5H, broad s, C_4-C_6H_5) All new compounds were synthesized in different ways
13) In contrast to the complicated reaction described above, the reaction of 1 with phenylmagnesium bromide yielded only 3 (51 %)[11] and the reaction of 10-aryl-9-phenylthioxanthenium salt with phenyllithium gave 9-aryl-9-phenylthioxanthene and 3 in good yields [4] In the latter reaction no rearrangement of the group on the sulfur atom to the aromatic ring was observed
14) The mass spectrum of a raw product obtained from radical phenylation of 3 showed a peak at m/e 426 Details of the reaction will be reported in a full paper
15) It is supposed that these compounds are formed by the scheme shown below (see Ref 2)

$$2\ \underline{\underline{10}} \xrightarrow{C_6H_5} M^+\ \underset{\text{(Isomers)}}{622} \xrightarrow{2C_6H_5} M^+\ 774 \xleftarrow{C_6H_5} M^+\ 698 \xleftarrow{C_6H_5} \underline{\underline{7}}$$

16) The results will be described in a full paper
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