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10-Thiaänthracenes. I. Mechanism of the Reaction of 9-Phenylthioxanthylium Salt with Organometallic Reagents[1]

Mikio Hori, Tadashi Kataoka,[2a] Yutaka Asahi, and Eiji Mizuta[2b]

Gifu College of Pharmacy[2a] and Chemical Research Laboratories, Central Research Division, Takeda Chemical Industries, Ltd.[2b]

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9-Phenylthioxanthylium perchlorate (I) reacts under an N_2 stream with C_6H_5MgBr and CH_3MgI and gives 9,9-diphenylthioxanthene (II) and 9-methyl-9-phenylthioxanthene (IV), respectively, as main products. In the presence of air, 9-phenylthioxanthyl peroxide (III) is formed as a by-product by the reaction of I with C_6H_5MgBr. The mechanism of these reactions was clarified by the studies by the ESR technique. The spectrum of 9-phenylthioxanthyl radical (VI), which was a reaction intermediate, was analyzed by the McLachlan SCF-MO computation.

The electron spin resonance spectrum of VI was also observed by the formation of 9,10-diphenyl-10-thiaänthracene (V) by the reaction of I with C_6H_5Li.

In order to examine the mechanism of formation of thioxanthenes and thiaänthracenes, the chemical reactivity of VI was studied. VI reacted with iodine, air, and the solvents such as ether and THF to give XIII, III, and XII, respectively. It did not react with organometallic reagents such as Grignard reagents and C_6H_5Li but reacted with ether to give XII only. However, it gave IV and V by the reaction with CH_3MgI and C_6H_5Li, respectively, in the presence of $CoBr_2$.

These experimental results show that the radical mechanism considerably contributes to the reactions between I and organometallic reagents.

Several reports have been published on the reactions between organometallic reagents and sulfur-containing six-membered aromatic compounds. Grignard reagents react with the carbon atom at α- or γ-position of thiopyrylium salts and their benzo- and dibenzo-analogues to form corresponding thiopyran derivatives.[3,4a,b] However, alkyllithiums and aryllithiums react with thiopyrylium salts at different reaction points. Namely, alkyllithiums form the same products as Grignard reagents,[3a] but aryllithiums couple with sulfur in thiopyrylium salt to form so-called thiabenzenes, which contain a decet sulfur. Thiabenzenes are new aromatic heterocycles, which have been estimated to possess appreciable cyclic conjugation through the ylene-like structure.[4] The formation of thiabenzenes from thiopyrylium salts and aryllithiums is the largest difference between the reactivity of thiopyrylium salt and that of pyrylium salt.[5]

The authors closely examined the mechanism of the formation of thioxanthene or 10-thiaänthracene derivatives by the reactions of 9-phenylthioxanthylium perchlorate (I) with Grignard reagents and aryllithiums. The results will be reported below.

Chart 1 shows the results of reactions between I and Grignard reagents together with those between I and phenyllithium. When I was allowed to react with 5 equivalents of phenylmagnesium bromide or methylmagnesium iodide under a nitrogen stream, the reaction

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[1] A part of this work was presented at the Third Organic Sulfur Symposium, Caen (France), May, 1968. Abstracts of Papers, p. 91. M. Hori, T. Kataoka, H. Shimizu, and C. Hsü, *Chem. Letts.*, 391 (1973).

[2] Location: *a*) *492-36, Mitahora, Gifu*; *b*) *Juso-Nishino-cho, Higashiyodogawa-ku, Osaka.*

[3] *a*) G. Suld and C.C. Price, *J. Am. Chem. Soc.*, **84**, 2090 (1962); *b*) K. Dimroth, K. Wolf, and H. Kroke, *Ann.*, **678**, 183 (1964); *c*) A. Lüttringhaus, N. Engelhard, and A. Kolb, *Ann.*, **654**, 189 (1962).

[4] *a*) C.C. Price and D.H. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969); *b*) G. Suld and C.C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961); *c*) *Idem, ibid.*, **84**, 2094 (1962); *d*) C.C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963).

[5] M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.* (Tokyo), **21**, 1318 (1973).

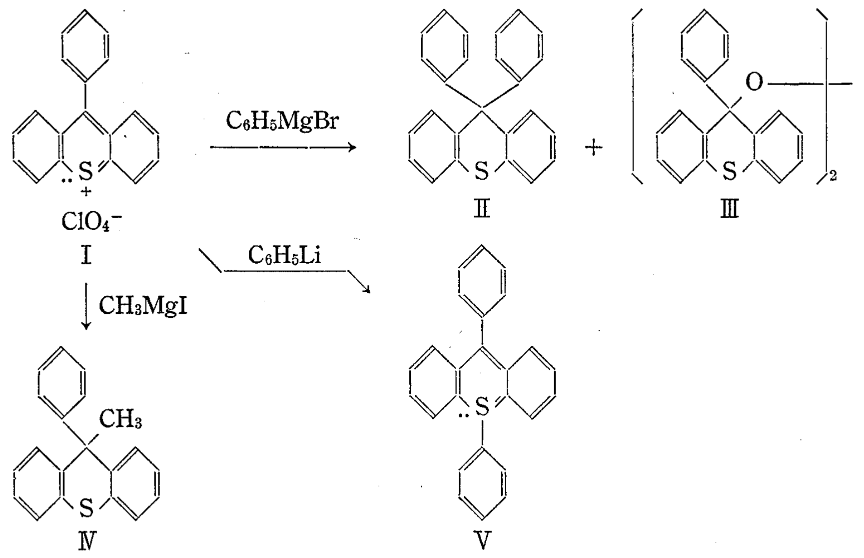


Chart 1

took place at 9-position to form 9,9-diphenylthioxanthene (II) or 9-methyl-9-phenylthioxanthene (IV) with a yield of 51% and 76%, respectively. When the reaction was allowed to proceed in air, 9-phenylthioxanthyl peroxide (III) was produced as a by-product. The structure of this product was determined by the data obtained by elemental analysis, nuclear magnetic resonance (NMR), and infrared (IR) spectra.

As in the case of the reaction between Grignard reagents and 9-phenylxanthylium salt, which is an oxygen compound corresponding to I, it is well expected from the formation of III that a radical intermediate is present in the above reaction.5)

Price, Hori, *et al.*4d) noticed ESR signals with some remarkable fine structures in the synthesis of 9,10-diphenyl-10-thiaänthracene (V) from I and phenyllithium. However, the signal has not been studied in further detail. Therefore, the authors now performed the election spin resonance (ESR) spectroscopic study on the radical as a reaction intermediate as well as on the chemical reactivity of the radical. The results will be described below.

Study on the Reaction of I with Organometallic Reagents by ESR Measurement

When I was allowed to react in the absence of oxygen with various Grignard reagents and phenyllithium in ether or with zinc or potassium in THF at room temperature, almost the same ESR spectra with a hyperfine structure were obtained. The intensity of the spectra showed that the concentration was as high as 3% immediately after the reaction and that the concentration then gradually decreased. Fig. 1 shows the ESR spectrum.

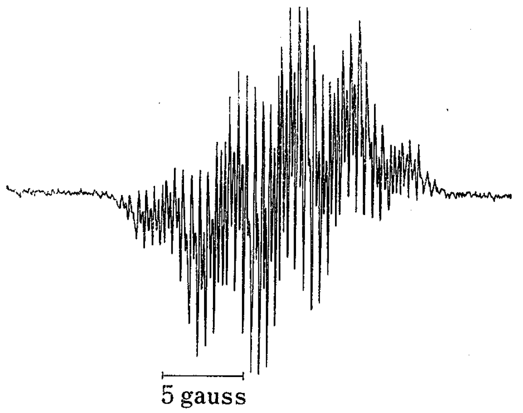


Fig. 1. ESR Spectrum of 9-Phenylthioxanthyl Radical (VI)

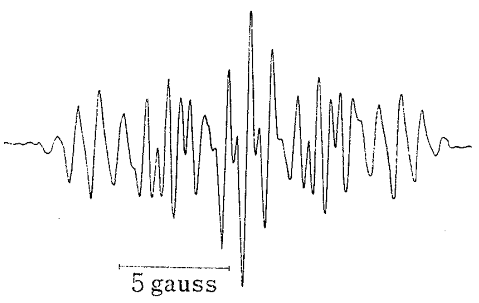
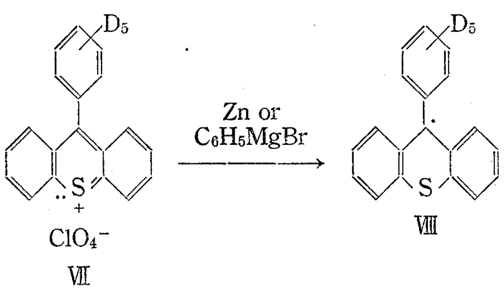


Fig. 2. ESR Spectrum of 9-Phenyl(-d_5)-thioxanthyl Radical (VIII)

These ESR spectra were analyzed as follows on the assumption that radical VI is formed as an intermediate: By the reaction of 9-phenyl(-d_5)-thioxanthylium salt (VII) and phenylmagnesium bromide in ether[6] or by the reaction of VII and zinc in THF, the simple ESR spectrum of 9-phenyl(-d_5)-thioxanthyl radical (VIII) was obtained as shown in Fig. 2. By the comparison with the results of analysis of VIII as shown in Table II, hyperfine splitting constants of VI were estimated by the trial-and-error method from the odd electron densities ρ_i, which requires that $A_{iH}=-Q\rho_i$ in gauss. A_{iH} and ρ_i were calculated by the McLachlan SCF-MO computation.[7] The ESR spectra of radical VI calculated from these values were close to experimental spectra. Therefore, radical VI was identified as 9-phenylthioxanthyl radical.



The ESR spectrum of this radical VI was very similar to that of the radical obtained by Maruyama, *et al.*[8] from 9-phenylthioxanthyl chloride by the Gomberg method.[9] The spectrum also coincided with the ESR spectrum of a mixture of I and zinc in methylcyclohexane, which was obtained at −65° by Lunazzi, *et al.*,[10] very recently. Table I summarizes the

Table I. Odd Electron Densities (ρ_i) by MO Calculation and Proton Hyperfine Splitting Constants ($|A_{iH}|=-Q\rho_i$ in gauss) of 9-Phenylthioxanthyl Radical (VI)

Position	Reference						
	Present work			Lunazzi, *et al.*			Maruyama, *et al.*
	ρ_i	$\lvert A\rvert_{calcd.}$	$\lvert A\rvert_{obs.}$[a]	ρ_i	$\lvert A\rvert_{calcd.}$	$\lvert A\rvert_{obs.}$	$\lvert A\rvert_{obs.}$
1, 8	0.120	3.24	3.22[b]	0.1467	3.81	3.24[b]	3.28
2, 7	−0.042	1.13	0.98	−0.0467	1.21	1.03	0.47
3, 6	0.113	3.05	3.71[b]	0.1151	2.99	3.77[b]	3.10
4, 5	−0.040	1.08	0.98	−0.0296	0.77	0.95	0.47
4a, 10a	0.1171			—			
8a, 9a	0.0527			—			
9	0.4680			0.5311			
10	0.0818			0.0305			
1′	−0.0066			—			
2′, 6′	0.012	0.32	1.47	0.0122	0.32	0.52	0.95
3′, 5′	−0.005	0.13	0.5	−0.0044	0.11	0.06	—
4′	0.012	0.32	1.27	0.0133	0.35	0.24	1.16
θ[c]		72°		72°			—
Temperature	room temperature			−65°			room temperature
g-value	2.0033			2.00437			—
−Q	27			26			—
Parameters	$\alpha_s=\alpha+0.9\beta$, $\alpha_{adj.}=\alpha+0.1\beta$, $\beta_{C-S}=0.5\beta$, $\lambda=1.2$			$\alpha_S=\alpha+1.2\beta$, $\beta_{C-S}=0.65\beta$			—

a) The ESR spectra were measured on a Universal-Cavity TE_{105} of 3B type spectrometer manufactured by Japan Electron Optics Lab. Co., Ltd.

b) In analogy with 9-phenylxanthyl radical, $A_{3,6H(obs.)}$ can be assigned to a larger value than $A_{1,8H(obs.)}$, though $A_{1,8H(calcd.)}$ is larger than $A_{3,6H(calcd.)}$ according to the results of MO calculation. Refer to M.D. Sevilla and G. Vincow, *J. Chem. Phys.*, **72**, 3641 (1968) and literature 5).

c) Angle between the plane of the 9-phenyl group and that of the thioxanthyl moiety: by the relation $\beta_{9-1'}=\beta\cos\theta$.

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6) M. Hori, T. Kataoka, and M. Ban, "Unpublished results."

7) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960); A.D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

8) K. Maruyama, M. Yoshida, and K. Murakami, *Bull. Chem. Soc. Japan*, **43**, 152 (1970).

9) M. Gomberg and L.H. Cone, *Ann.*, **376**, 201 (1910).

10) L. Lunazzi, A. Mangini, G. Placucci, and C. Vincenzi, *Mol. Phys.*, **19**, 543 (1970).

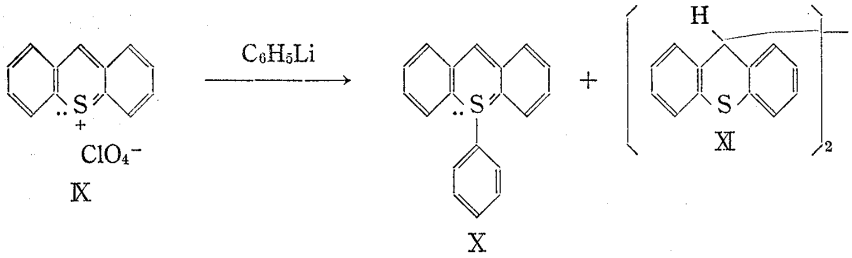
Table II. Proton Hyperfine Splitting Constants ($|A_{iH}|$) of 9-Phenyl(-d_5)-thioxanthyl Radical (VIII)

Formation type		Position				θ	Temperature
		1, 8	2, 7	3, 6	4, 5		
VII+Zn in THF	$\lvert A\rvert_{obs.}$	3.18[a]	0.99	3.77[a]	0.99	72°	room temperature
VII+C_6H_5MgBr in ether	$\lvert A\rvert_{obs.}$	3.15[a]	1.01	3.76[a]	1.01	72°	room temperature

[a] See Table I. footnote *b*).

results of analysis of the ESR spectrum of VI obtained by three different methods.

On the other hand, Price, Hori, *et al.*[4d] reported that they obtained bithioxanthyl (XI) with a yield of 14% besides 10-phenyl-10-thiaanthracene (X) by the reaction between thioxanthylium perchlorate (IX) and phenyllithium. This result is explained by the mechanism



as shown in Chart 2. However, experimental results show that phenol is not formed. Therefore, it is likely that a radical mechanism is related to the reaction between I and organometallic compounds to a considerable degree besides the ionic mechanism.[11] Thioxanthyl radical is formed in this case as an intermediate.

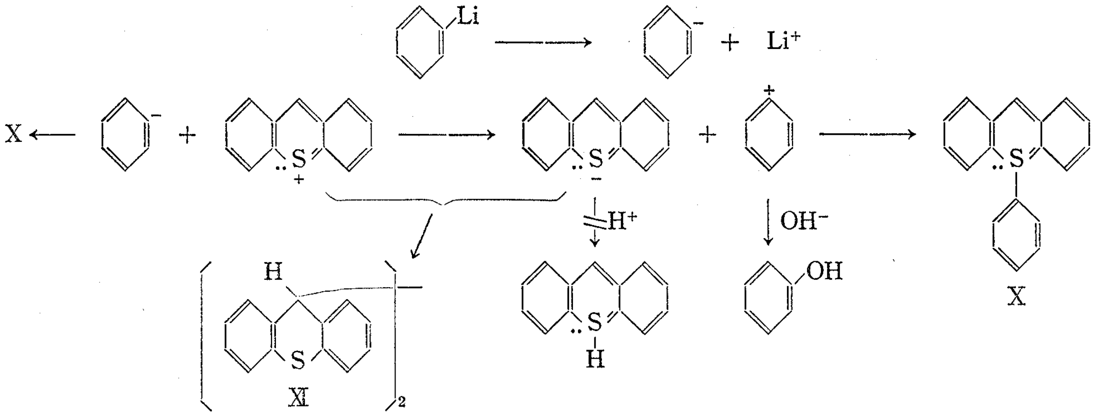


Chart 2

Chemical Reactivities of Stable Radical VI

From the reason as mentioned above, the authors then closely examined chemical reactivities of the stable radical VI. Results are as follows (Chart 3): For the synthesis of

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[11] Syntheses of 10-aryl-10-thiaänthracenes, except for the reactions between thioxanthylium salts and aryllithiums, have not been made entirely successful until now. Reactions of 10-alkyl- or 10-arylthioxanthenium salts with strong bases, such as sodium hydride or phenyllithium in a suitable solvent, are explained as ionic reactions by the ESR measurement. In this case 10-alkyl- or 10-arylthioxanthenium salts showed smooth conversion into 9-alkyl- or 9-arylthioxanthenes instead of the formation of 10-alkyl- or 10-arylthiaänthracenes. Details will be published elsewhere by M. Hori, T. Kataoka, and H. Shimizu.

radical VI, the reduction of I with zinc was performed in THF, because this procedure was simple to perform.[12] Although radical VI was stable, it abstracted hydrogen from ether to form 9-phenylthioxanthene (XII) and also formed peroxide III with a yield of 41% when dry air was blown into it. VI also reacted with an ethereal solution of iodine to form 9-phenylthioxanthylium triiodide (XIII), with a yield of 70%. Against organometallic reagents, VI reacted with none of phenylmagnesium bromide, methylmagnesium iodide, and phenyllithium but reacted with the solvent to form XII only as mentioned above. However a similar reaction gave different results depending upon the kind of the reagent in the presence of cobaltous bromide, which caused a radical reaction of Grignard reagents.[13] When VI was allowed to react with phenylmagnesium bromide in the presence of cobaltous bromide, expected products were not formed, and XII only was formed. However, 9,10-diphenyl-10-thiaänthracene (V) was formed with a yield of 13% in the case of phenyllithium. This difference in the reactivity is explained as follows: The reaction between phenylmagnesium bromide and cobaltous bromide takes place in a solvent cage resulting in the formation of biphenyl only. The phenyl radical formed by the reaction between phenyllithium and cobaltous bromide couples with VI outside the solvent cage and gives V. This explanation well agrees with the result of the reaction of 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone with phenylmagnesium bromide and with phenyllithium, which was reported by Relles in 1969.[14]

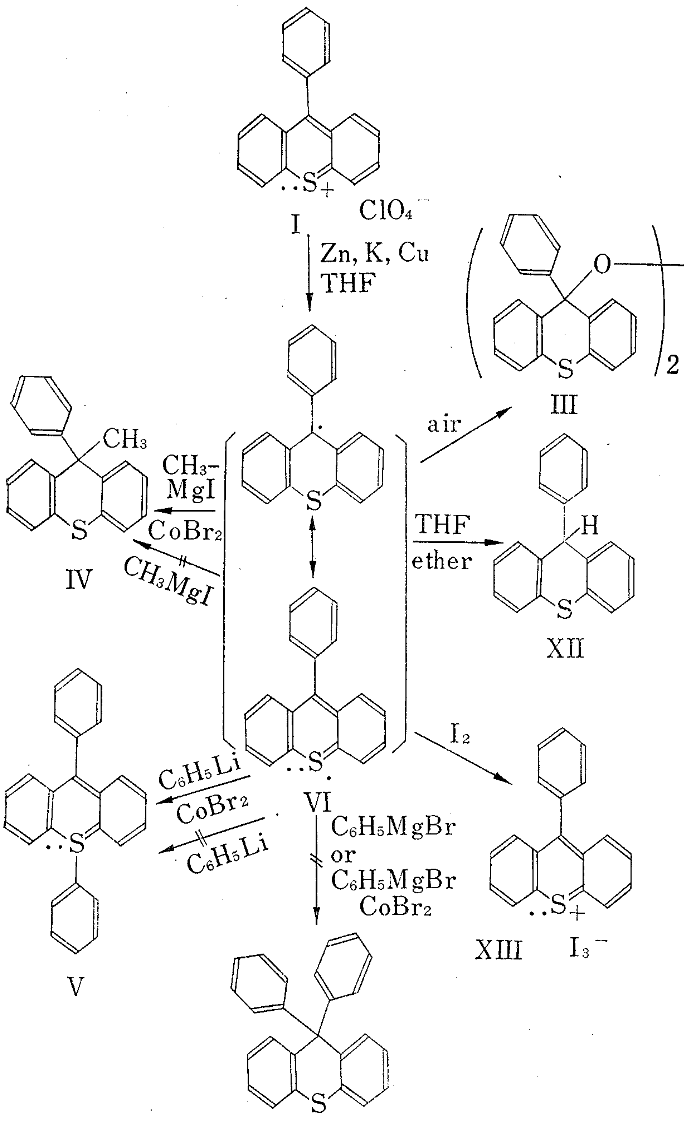

Chart 3

On the other hand, the reaction of methylmagnesium iodide with VI gave IV in the presence of cobaltous bromide with a yield of 30%. Therefore, it was found that the reaction took place outside the solvent cage contrary to the reaction of phenylmagnesium bromide.

Mechanism of the Reaction of I with Organometallic Reagents

Summarizing the results mentioned above, the authors propose a mechanism as shown in Chart 4 for the reaction between I and organometallic reagents. The reaction between

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12) One electron reduction of I with zinc, sodium dithionite, *etc.* in diglyme was also reported by C.C. Price, M. Siskin, and C.K. Miao, *J. Org. Chem.*, **36**, 794 (1971).

13) M.S. Kharasch, R.D. Mulley, and W. Nudenberg, *J. Org. Chem.*, **19**, 1477 (1954); F.W. Frey, Jr., *J. Org. Chem.*, **26**, 5187 (1961).

14) H.M. Relles, *J. Org. Chem.*, **34**, 3687 (1969).

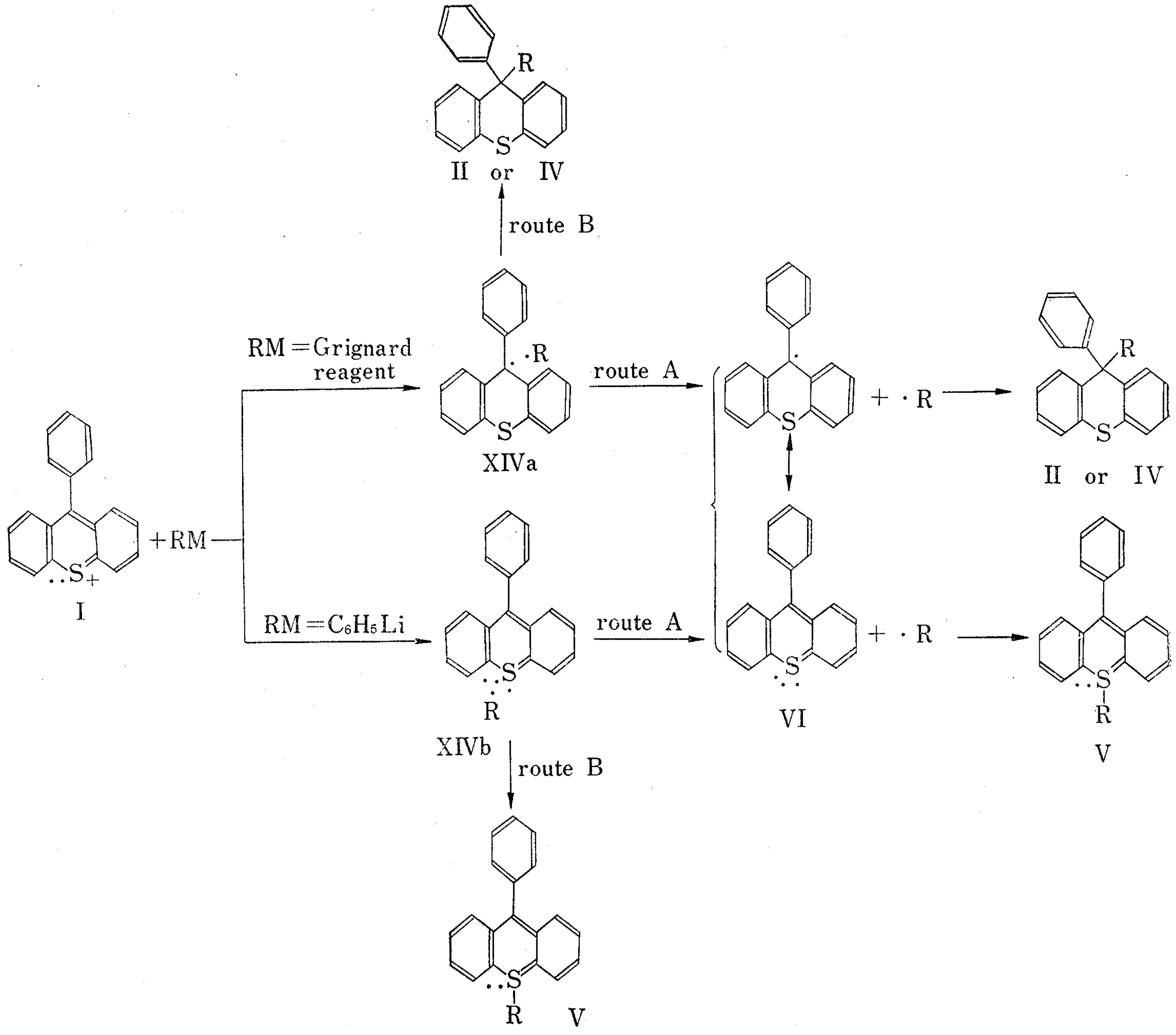

Chart 4

I and an organometallic reagent RM forms a radical pair XIV. By this formation, it is estimated that a radical pair takes the XIVa type against Grignard reagents, but takes the XIVb type against phenyllithium. In the case of phenylmagnesium bromide, XIVa forms II only by route B. In the case of methylmagnesium iodide, IV is mainly formed through route B. IV is partly formed through route A. On the other hand, the main route of XIVb is B as in the case of methylmagnesium iodide, and partly forms V through route A. The positions of reaction of VI are 9 and 10. The values of the densities of odd electron, ρ, are 0.4680 and 0.0818, respectively. However, a question still remains to be solved in the future why phenyllithium only couples with the positive sulfur of I to form thiaänthracene derivatives.

Experimental[15]

Reaction of 9-Phenylthioxanthylium Perchlorate (I) with Phenylmagnesium Bromide——a) I[4d] (3.8 g, 10 mmole) was added to an ethereal solution of C_6H_5MgBr prepared from bromobenzene (8.0 g, 50 mmole) and Mg (1.4 g, 60 mmole). After stirring for 2 hr at room temperature the reaction mixture was decomposed

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15) All melting points were measured with a Yanagimoto micromelting point apparatus and uncorrected. NMR spectra were measured with a Hitachi R-20B using tetramethylsilane as an internal standard.

with a cold NH_4Cl solution and extracted with ether. The extract was dried and evaporated. The treatment of the residue by column chromatography on silica gel using benzene–pet. ether (1:1) gave following two compounds. 9,9-Diphenylthioxanthene (II) was recrystallized from benzene–pet. ether to give 1.5 g of colorless prisms, mp 214° (reported[4d] 218°). *Anal.* Calcd. for $C_{25}H_{18}S$: C, 85.67; H, 5.18. Found: C, 85.71; H, 5.24. NMR (CCl_4) τ: 2.5—3.4 (18H, multiplet, aromatic H). 9-Phenylthioxanthyl peroxide (III) was recrystallized from benzene to give 0.2 g of colorless plates, mp 189° (decomp.) (reported[16] 188° (decomp.)). *Anal.* Calcd. for $C_{38}H_{26}O_2S_2$: C, 78.86; H, 4.53. Found: C, 78.97; H, 4.78.

b) I (1.5 g, 4 mmole) was treated with C_6H_5MgBr prepared from bromobenzene (3.1 g, 20 mmole) and Mg (0.5 g, 21 mmole) under an N_2 stream. The same treatment as a) afforded II (0.72 g) and a substance, mp>300° (trace), which has main peaks at *m/e*: 546 (M^+), 273 (9-phenylthioxanthyl) in the mass spectrum and no characteristic absorptions in the IR spectrum. The latter was assumed to be 9,9′-diphenylbithioxanthyl.

Reaction of I with Methylmagnesium Iodide——I (0.76 g, 2 mmole) was added to an ethereal solution of CH_3MgI prepared from methyl iodide (1.4 g, 10 mmole) and Mg (0.3 g). The reaction mixture worked up as before gave crude 9-methyl-9-phenylthioxanthene (IV), which was recrystallized from MeOH to give 0.44 g of colorless needles, mp 137°. *Anal.* Calcd. for $C_{20}H_{16}S$: C, 83.28; H, 6.99. Found: C, 83.38; H, 5.52. NMR ($CDCl_3$) τ: 2.36—3.34 (13H, multiplet, aromatic H), 8.00 (3H, singlet, CH_3).

Reaction of 9-Phenylthioxanthyl Radical (VI) with Air——Dry air was passed through a stirred suspension of I (1 g) and Zn powder (0.5 g) in THF (15 ml) for 5 hr. The precipitate was filtered and washed with benzene thoroughly. After the filtrate was evaporated, the resulting residue was dried. Preparative TLC on silica gel produced 9-phenylthioxanthyl peroxide (III) (0.32 g), 9-phenylthioxanthenol (0.03 g), and thioxanthone (0.01 g). These compounds were identified by mixed melting point tests and comparison of IR spectra with those of authentic samples.

Hydrogen Abstraction by VI from Ethyl Ether——A suspension of I (1.00 g) and Zn powder (0.7 g) in THF (35 ml) was stirred for 1.5 hr under an N_2 stream, and then added with anhydrous ether (35 ml). Stirring was continued for a day, and dry air was passed through the reaction mixture to convert remaining VI into peroxide III. After removal of the solvent, the residue was washed with ether. Evaporation of the ether washings afforded 9-phenylthioxanthene (XII) (0.44 g), mp 99° (reported[4d] 99°), which was recrystallized from pet. ether as colorless prisms. An ether-insoluble material was extracted with benzene. Removal of the solvent gave III (0.2 g).

Reaction of VI with Iodine——VI was prepared from I (1 g) and Zn powder (1 g) as mentioned above and excess Zn and zinc perchlorate were filtered off. To the resulting red-brown radical solution iodine (1 g) in ether (100 ml) was added. After 2 hr at room temperature, the solvent was removed under reduced pressure. The residue was recrystallized from AcOH to give 9-phenylthioxanthylium triiodide (XIII) (1.2 g) as dark red plates, mp 272° (decomp.). *Anal.* Calcd. for $C_{19}H_{13}SI_3$: C, 34.88; H, 2.00. Found: C, 35.01; H, 1.98.

Reactions of VI with Organometallic Reagents, CH_3MgI, C_6H_5MgBr, and C_6H_5Li——To a filtered solution of VI prepared from I (1.8 g, 5 mmole) and Zn powder (0.5 g) in THF (35 ml) as mentioned above, the organometallic reagent (25 mmole) was added under an N_2 atmosphere. After reacting for a day, the reaction mixture was decomposed with a cold NH_4Cl solution and extracted with ether. The ether extract was dried and evaporated. The resulting residue was chromatographed on silica gel to give XII (0.48—0.51 g) and III (*ca.* 0.02 g).

Reaction of VI with CH_3MgI in the Presence of $CoBr_2$——To a filtered solution of VI prepared from I (2 g) and Zn powder (2 g) in THF (50 ml), an ethereal solution of CH_3MgI prepared from methyl iodide (3.8 g) and Mg (0.7 g) was added under an N_2 stream. Anhydrous $CoBr_2$ (0.1 g) was then added. After standing for 2 days the reaction mixture worked up in the usual manner gave 9-methyl-9-phenylthioxanthene (IV) (0.4 g) and a small amount of III.

Reaction of VI with C_6H_5MgBr in the Presence of $CoBr_2$——To an ethereal solution of C_6H_5MgBr prepared from bromobenzene (4 g) and Mg (0.8 g) containing a small amount of $CoBr_2$, a filtered solution of VI prepared from I (1.87 g) and Zn powder (0.5 g) was added under an N_2 stream. After standing for 5 hr the reaction mixture worked up as mentioned above gave XII (0.79 g).

Reaction of VI with C_6H_5Li in the Presence of $CoBr_2$——To an excess of C_6H_5Li solution under an N_2 stream, a filtered solution of VI prepared from I (1.86 g) and Zn powder (0.5 g) in THF (50 ml) were added. Anhydrous $CoBr_2$ (0.1 g) was then added. After standing for 3 hr the reaction mixture was treated by the usual thiabenzene synthetic method to give 9,10-diphenyl-10-thiaanthracene (V) (0.23 g) as a brown powder. This compound had the same IR, NMR, and mass spectra as those of an authentic sample.

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16) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, **1945**, 657.

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