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Reactions of 9-Phenylxanthylium Salts with Organometallic Reagents. I[1]

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A close examination was made on the reactions between 9-phenylxanthylium salt (I) and various Grignard reagents, such as C_6H_5MgBr, *o*- and *p*-$CH_3OC_6H_4MgBr$, and CH_3MgI. It was found that the 9-phenylxanthyl radical (IX) is formed in these reactions as an intermediate; from which 9-phenyl-9-substituted xanthenes are formed. 9-Phenylxanthenes V and VIII, which are derived from IX, are formed simultaneously.

The electron spin resonance spectrum of the radical IX was analyzed by the McLachlan SCF-MO computation.

Mechanism of the reaction of I with Grignard reagents were discussed in detail.

The reaction between II and Grignard reagents gave the products similar to those of the reaction between I and Grignard reagents.

It was confirmed that radical routes are related with the reaction mechanism to a considerable extent.

There have been several reports on the reactions between organometallic reagents and oxygen-containing six-membered aromatic compounds, such as pyrylium salts and their benzo- and dibenzo-analogues.[3,4] The reaction generally takes place in oxygen-containing rings to give a pyran derivative, except the case of pyrylium salt. In the case of pyrylium salt, an addition reaction occurs followed by ring opening. Ziegler, *et al.*[4d] reported on the formation of 9-phenylxanthyl radical from 9-phenylxanthylium perchlorate (I) and phenylmagnesium bromide but did not describe on the final reaction products. Schoepfle, *et al.*[5] studied in 1937 on the reaction between 9-phenylxanthyl chloride (II) and phenylmagnesium bromide and obtained 3,9-diphenylxanthene (III) (51%), 3,6,9-triphenylxanthene (IV) (14%), 9-phenylxanthene (V) (19%), and 9,9-diphenylxanthene (VI) in traces as shown in Chart 1.

The present authors closely examined the reactions between Grignard reagents and I, which presumably shows the same reactivity as II, and obtained following result (Chart 2). Under a nitrogen stream, I was allowed to react with phenylmagnesium bromide, the molar ratio between phenylmagnesium bromide and I being the same as that of Schoepfle, *et al.* Although VI (36%) and V (23%) were obtained as reaction products (III and IV), which are the products expected from the results of Schoepfle, *et al.*, were not obtained. It was also found that VIII is produced as a by-product when the reaction is conducted in air.

By the reaction between I and Grignard reagents, an electron spin resonance (ESR) spectrum with hyperfine structures was observed as shown in Fig. 1. This spectrum suggests that

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1) A part of this work was presented at Third Organic Sulfur Symposium, Caen (France), May 1968. Abstracts of Papers, p. 91.

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

3) *a*) G. Köbrich, *Angew. Chem.*, **72**, 348 (1960); *b*) G. Köbrich and D. Wunder, *Ann.*, **654**, 131 (1962); *c*) K. Dimroth and G. Neubauer, *Chem. Ber.*, **92**, 2042 (1959); *d*) K. Dimroth and K. H. Wolf, *Angrew. Chem.*, **72**, 777 (1960); *e*) K. Dimroth, K.H. Wolf, and H. Kroke, *Ann.*, **678**, 183 (1964).

4) *a*) A. Löwenbein, *Chem. Ber.*, **57**, 1517 (1924); *b*) A. Löwenbein and B. Rosenbaum, *Ann.*, **448**, 223 (1926); *c*) K. Ziegler, *Ann.*, **434**, 34 (1923); *d*) K. Ziegler and C. Ochs, *Chem. Ber.*, **55**, 2257 (1922); *e*) M. Gomberg and L.H. Cone, *Ann.*, **370**, 142 (1909).

5) C.S. Schoepfle and J.H. Truesdail, *J. Am. Chem. Soc.*, **59**, 372 (1937).

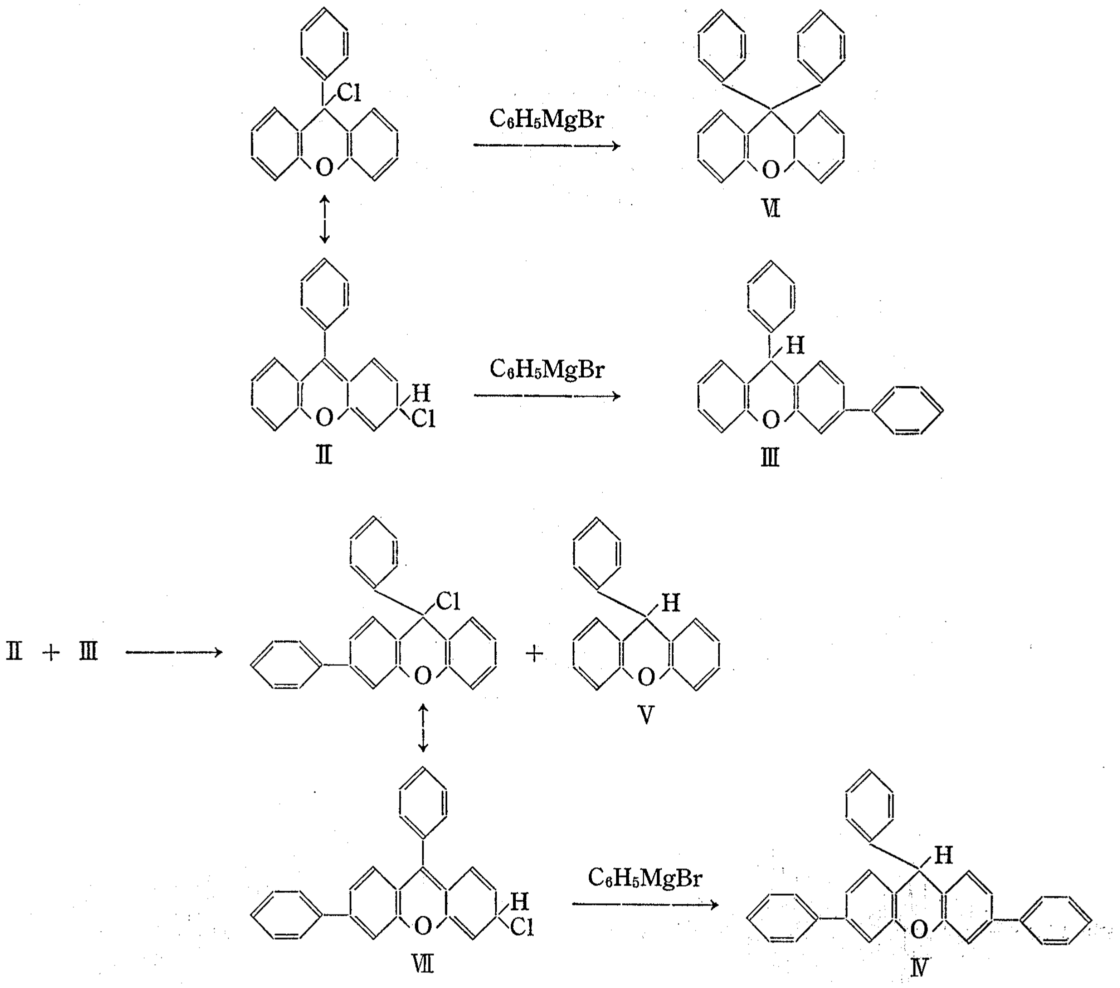

Chart 1

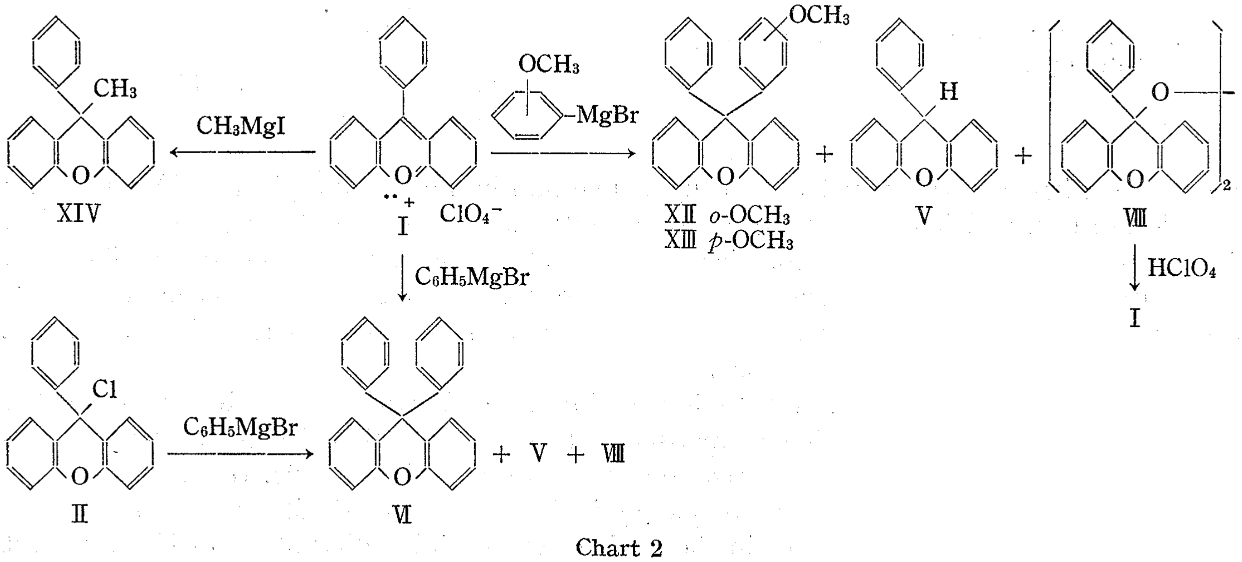

Chart 2

the radical might be an intermediate of the reaction. The same spectrum was also observed by the treatment of I with zinc powder or potassium in THF. The ESR spectrum of this radical was also very similar to that of radical IX obtained by Sevilla, *et al.*[6] and Maruyama,

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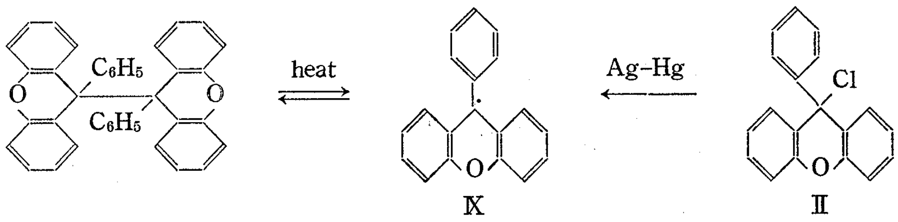
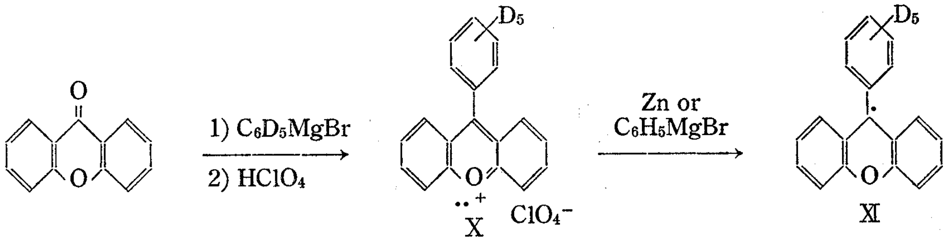
6) M.D. Sevilla and G. Vincow, *J. Chem. Phys.*, **72**, 3641 (1968).

et al.[7] by the two different methods shown below, namely, by the homolytic dissociation and the Gomberg reaction,[4e] respectively. It was further found that the hyperfine splitting constants of the observed ESR spectrum well agreed with those calculated by the McLachlan SCF-MO computation for 9-phenylxanthyl radical.[8] Thus IX was identified with 9-phenylxanthyl radical. The assignment of the radical IX was further confirmed by the observation of ESR spectrum of 9-phenyl(-d_5)xanthyl radical (XI) (Fig. 2 and Table II) obtained by





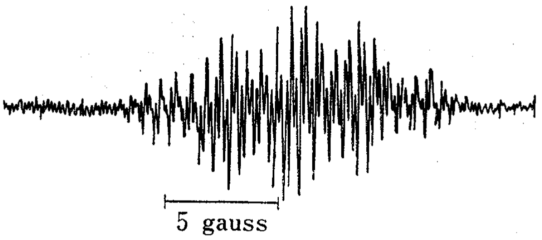


Fig. 1. ESR Spectrum of 9-Phenylxanthyl Radical (IX)

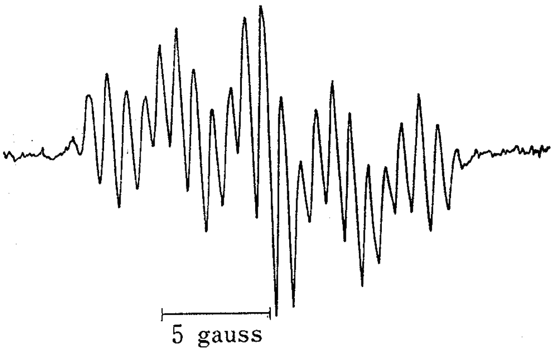


Fig. 2. ESR Spectrum of 9-Phenyl(-d_5)-xanthyl Radical (XI)

the reaction between zinc powder or phenylmagnesium bromide and 9-phenyl(-d_5)xanthylium perchlorate (X), which was synthesized from xanthone and phenyl(-d_5)magnesium bromide. The results are shown in Table I together with the data by Maruyama, *et al.* and Sevilla, *et al.* for comparison. Although a little difference is recognized among the three calculated values, the tendency of the values is in accord with one another. Consequently, it is evident that the three radicals are just the same one.

The results of the reaction of phenylmagnesium bromide with I were different from that with II beyond expectation. The comparison of these two reactions led the authors to confirm following points by the reinvestigation of the results of Schoepfle, *et al.*

(i) The O-ClO_4 bonding of I is completely ionic, whereas the C_9-Cl bonding in II is considerably covalent. This difference in the mode of chemical bonding of I and II may affect the chemical reaction in some way.

(ii) Each of the reaction mixture is dark green in color. This coloration suggests that the intermediacy of both reactions may be the same.

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

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

Table I. Odd Electron Densities (ρ_i) by MO Calculation and Proton Hyperfine Splitting Constants ($|A_{iH}|=-27\,\rho_i$ in gauss) of 9-Phenylxanthyl Radical (IX)

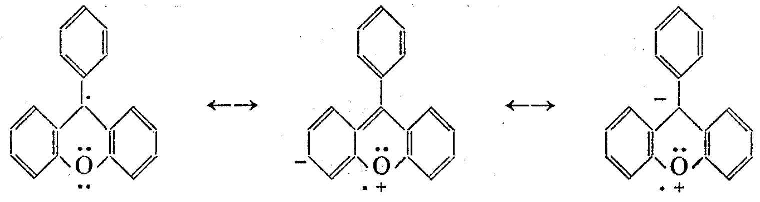
Reference	Present work			Sevilla, *et al.*			Maruyama, *et al.*		
position	ρ (McLachlan SCF-MO)	$\|A\|_{calcd.}$	$\|A\|_{obs.}$[a]	ρ (McLachlan SCF-MO)	$\|A\|_{calcd.}$	$\|A\|_{obs.}$	ρ (Hückel MO)	$\|A\|_{calcd.}$	$\|A\|_{obs.}$
1, 8	0.1256	3.38	3.34[b]	0.132	3.57	3.34[b]	0.09036	2.44	2.65
2, 7	−0.0453	1.22	0.83	−0.040	1.08	0.86	—	—	0.60
3, 6	0.1200	3.24	3.94[b]	0.111	3.00	3.81[b]	0.08094	2.18	2.60
4, 5	−0.0453	1.22	0.83	−0.029	0.78	0.74	—	—	0.64
4a,10a	0.1250			—			—		
8a, 9a	−0.0552			—			—		
9	0.4857			—			0.32540		
10	0.0319			—			—		
1′	−0.0107			—			—		
2′,6′	0.0198	0.53	0.60	0.030	0.81	0.74	—	—	0.55
3′,5′	−0.0076	0.21	0.20	0.010	0.27	0.61	—	—	0.91
4′	0.0188	0.52	0.83	0.030	0.81	0.86	0.02369	0.64	0.55
θ[c]	*ca.* 60°			60°			63°		
Temperature	room temperature			−60°			room temperature		
g-Value	2.0027			2.00289			—		
Parameters	$\alpha_O=\alpha+2\beta$, $\alpha_{adj.}=\alpha+0.2\beta$, $\beta_{O-C}=0.6\beta$, $\lambda=1.2$			$\alpha_O=\alpha+2\beta$, $\beta_{O-C}=0.75\beta$, $\lambda=1.1$			$\alpha_O=\alpha+1.3\beta$, $\beta_{O-C}=1.5\beta$		

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) Sevilla, *et al.*[6] confirmed by the studies of ESR of 3-deuterio derivative that $A_{3,6\,H(obs.)}$ can be assigned to a larger value than $A_{1,8\,H(obs.)}$, though $A_{1,8\,H(calcd.)}$ is larger than $A_{3,6\,H(calcd.)}$ according to the results of MO calculation.
Accordingly, the authors adopted this result and exchanged the value for $A_{1,8\,H(obs.)}$ with that of $A_{3,6\,H(obs.)}$. Thus the spectra of IX and XI were assigned.

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

d) The contribution of the resonance equation (IX′) must be very small because the values of ρ_{10} is very small.



IX IX′[d]

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

Position	1, 8	2, 7	3, 6	4, 5	θ	Temperature
$\|A\|_{obs.}$	3.15[a]	0.83	3.97[a]	0.83	60°	room temperature

a) See Table I footnote *b*).

(iii) Schoepfle, *et al.*[5] considered that the product (III) forms V and VII by the reaction with II. However, it is not reasonable that a considerably large difference is present between the pK_{R+} values of II and VII. It is doubtful that the reaction takes place between II and III to form V and VII.

(iv) Gomberg, *et al.*[4e] also quantitatively obtained 9-benzyl-9-phenylxanthene by the reaction between I and benzylmagnesium chloride. Thus Schoepfle's conclusion may not be correct.

Chart 2 shows the results of the reaction between II and phenylmagnesium bromide in a nitrogen stream. The same products as in the case of I were obtained in the same ratio.

The formation of III and IV, obtained by Schoepfle, *et al.*, was not noticed. The structures of the products were determined by the comparative identification with authentic samples synthesized by alternative methods. ESR measurements of this reaction also indicated the formation of the same radical IX as in the case of I. It was also found experimentally that I couples with *o*- or *p*-methoxyphenylmagnesium bromide to introduce an aryl group to 9-position. Namely, no reaction was found to occur at 3- or/and 6-positions of the xanthene ring.

An alkyl Grignard reagent, CH_3MgI, was allowed to react with I. The ESR spectrum of the radical IX was also found in this case. The yield of 9-methyl-9-phenylxanthene (XIV) was 70%. Compound V was not formed by this reaction. This result is attributable to the large reactivity of the reagent CH_3MgI, which is sterically smaller than phenylmagnesium bromide.

Chart 3 shows the synthetic routes of authentic samples prepared for the identification of the reaction products. VI was synthesized by the dehydration ring closure of diphenyl-(*o*-phenoxyphenyl)methanol (XVI) in acetic acid by the addition of a few drops of concentrated sulfuric acid.⁹⁾ The compound XVI was prepared by the reaction of phenylmagnesium bromide with *o*-phenoxybenzophenone (XV), which was obtained by refluxing of *o*-chlorobenzophenone and sodium phenolate in DMF. Specimens XII and XIII were synthesized by the ring closure by the same method as above after the completion of the reactions between XV and *o*- and *p*-methoxyphenylmagnesium bromide. The authors also synthesized specimen XVIII by the same method as above, because Schoepfle, *et al.*⁵⁾ expected the Grignard coupling with the *para* position of a phenyl group at 9-position, V was synthesized by the reduction

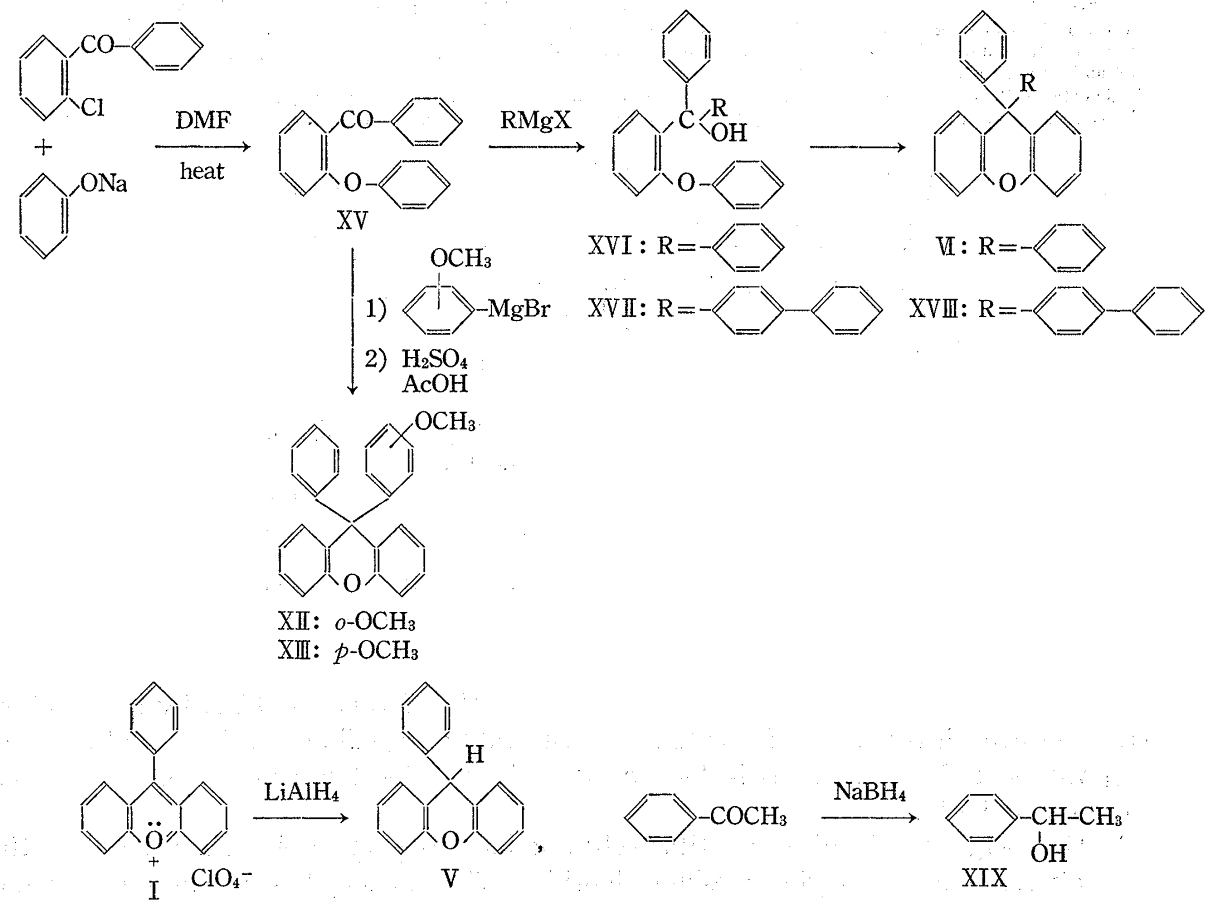


Chart 3

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9) F. Ullmann and G. Engi, *Chem. Ber.*, **37**, 2367 (1904).

of I with $LiAlH_4$. XIX was synthesized by the reduction of acetophenone with $NaBH_4$ in methanol.

Result and Discussion

With various Grignard reagents, I reacted at 9-position to generate the same radical IX as an intermediate and then formed VI or corresponding reaction products. Simultaneously, products V and VIII, which are derived from IX, were formed. The formation of IX was detected by the ESR measurement. The spectrum of IX was analyzed by theoretical calculation. The experimental result that the most active position of IX is 9-position was reasonably supported by the results of MO calculation (Refer to the odd electron densities, ρ_9, ρ_3 in Table I). It was also confirmed experimentally that the reaction between II and phenylmagnesium bromide gives the same result as the reaction of I; It was not possible to obtain III and IV, which are formed by the reaction at 3-or/and 6-positions of the xanthene ring, though Schoepfle, *et al.* obtained these. In this reaction, the presence of IX was confirmed by the ESR measurement. Now discussions will be made on the mechanism of the reactions between Grignard reagents and I and II based on the results of experiments mentioned above.

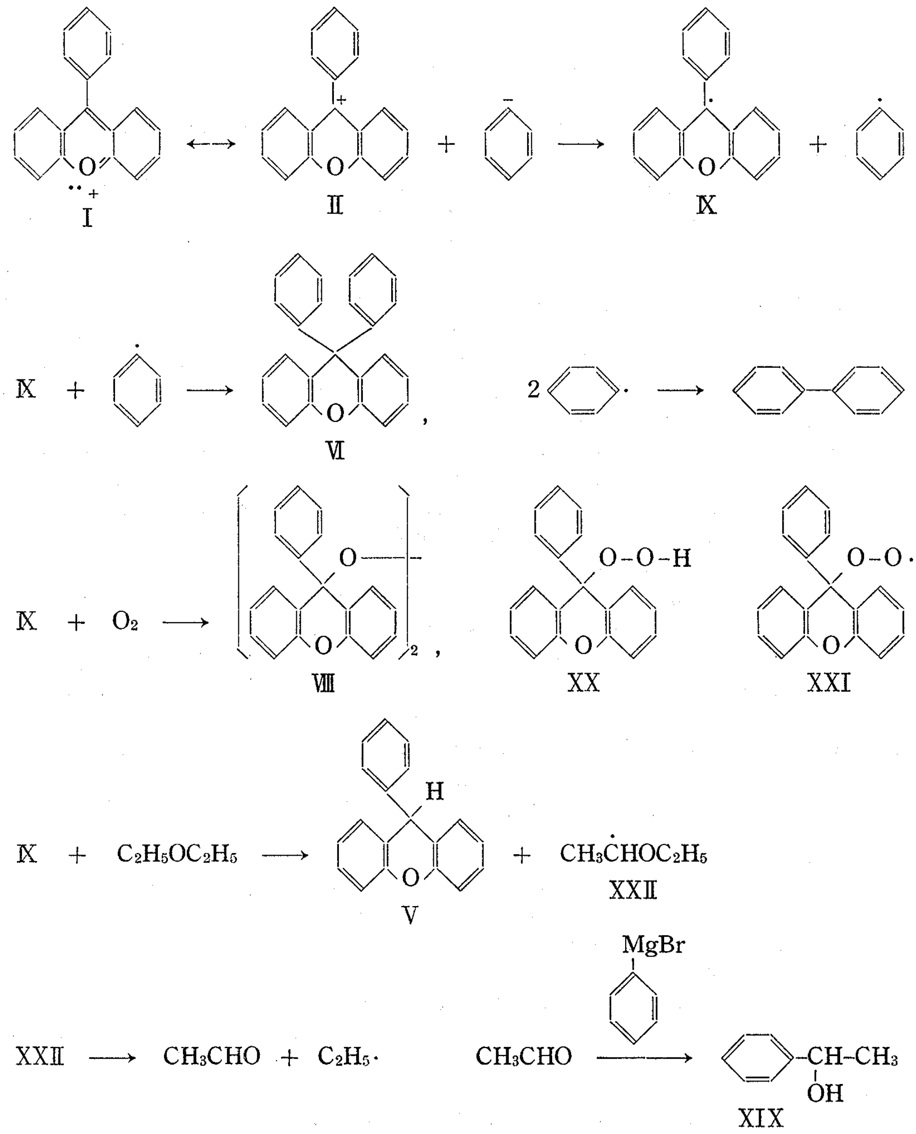

Chart 4

It was found that not only the ionic mechanism proposed by Schoepfle, *et al.* but also the radical mechanism as shown in Chart 4 is related with the reactions of Grignard reagents with I and II because (i) radical IX of high concentration was detected by the ESR measurements, and the concentration of the radical rapidly decreased within several minutes after the beginning of the reaction and (ii) VIII was formed by the reaction in air.[10] The formation of products in the title reactions is explained by the radical mechanism as follows: 9-phenylxanthylium ion reacts with phenyl carbanion to form IX and phenyl radical. The coupling between thse gives VI. The coupling between two phenyl radicals gives biphenyl. From IX and oxygen, VIII is formed. In this case, hydroperoxide XX is not formed because the concentration of peroxy free radical XXI, formed by the reversible reaction between oxygen and the stable radical IX, is relatively low and because the formation of VIII predominates in the presence of IX of high concentration. IX abstracts a hydrogen atom from the methylene group adjacent to the oxygen atom of ether, which is present as a solvent, and forms V. The unstable radical XXII thus formed spontaneously decomposes to form acetaldehyde, which reacts with phenylmagnesium bromide to give XIX. As phenylmagnesium bromide abstracts a hydrogen atom from ether,[11] the authors synthesized IX from I and zinc powder and confirmed that IX abstracts a hydrogen atom from ether to form V.

Studies are now being made on the reactions of other organometallitc compounds, such as phenyllithium, with I and II.

Experimental[12]

Reaction of 9-Phenylxanthylium Perchlorate (I) with Phenylmagnesium Bromide——a) An ethereal solution of phenylmagnesium bromide prepared from bromobenzene (1.6 g) and Mg (0.3 g) was added to a suspension of I[13] (0.9 g) in anhydrous ether under nitrogen. The color of the reaction mixture became dark green and then disappeared gradually. After stirring for 2 hr, the reaction mixture was decomposed with aqueous NH_4Cl and extracted with ether. The extract was dried and evaporated. The resulting residue was purified by column chromatography. Elution with benzene–pet. ether gave three compounds, 9-phenylxanthene (V), 9,9-diphenylxanthene (VI), and 9-phenylxanthyl peroxide (VIII). V was recrystallized from pet. ether to give 0.15 g of colorless prisms, mp 147° (reported[9] 145°). *Anal.* Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.38; H 5.47. VI was recrystallized from benzene–pet. ether to give 0.30 g of colorless prisms, mp 199° (reported[9] 200°). *Anal.* Calcd. for $C_{25}H_{18}O$: C, 89.79; H, 5.43. Found: C, 89.55; H, 5.32. VIII was obtained in mere trace amounts. These three compounds were identified by mixed melting point tests and IR spectra comparison with authentic samples. Elution with ether afforded 1-phenylethanol (XIX), which was distilled using microdistillation appearatus. Mass Spectrum *m/e*: 121 (M^+). NMR ($CDCl_3$) τ: 8.5 (3H, doublet, $J=6.8$ Hz, CH_3), 7.9 (1H, broad singlet, OH), 4.9 (1H, quartet, $J=6.8$ Hz, CH), 2.7 (5H, singlet, aromatic H). This sample was identified by IR and NMR spectra, and glc retention time comparison with an authentic sample.

b) To an ethereal Grignard solution prepared from bromobenzene (0.8 g) and Mg (0.2 g), I (0.8 g) was added. After stirring for 2 hr the reaction mixture was treated in the same way as a). V (0.10 g), VI (0.25 g), and VIII (0.11 g) were obtained. VIII was recrystallized from benzene to give colorless plates, mp 245—246° (decomp.) (reported[14] 230° (decomp.)). *Anal.* Calcd. for $C_{38}H_{20}O_4$: C, 83.49; H, 4.79. Found: C, 83.71; H, 4.99. XIX was also isolated and identified in the same way as a).

Reaction of 9-Phenylxanthyl Chloride (II) with Phenylmagnesium Bromide (Reinvestigation of Schoepfle's Experiment)——To an ethereal solution of phenylmagnesium bromide prepared from bromobenzene (1.6 g) and Mg (0.3 g) an ethereal solution of II (0.7 g) was added under nitrogen. The color of the solution

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10) By these reactions the authors obtained biphenyl and 1-phenylethanol. However, these are formed when phenylmagnesium bromide is synthesized in ether and then decomposed with water.[11] Therefore, the formation of these substances dose not necessarily prove that the reactions of Grignard reagents with I and II are radical reactions.

11) C. Walling and S.A. Buckler, *J. Am. Chem. Soc.*, **77**, 6032 (1955).

12) Melting points were measured on a Yanagimoto micromelting apparatus and uncorrected. The nuclear magnetic resonance (NMR) spectra were recorded on a Hotachi R-20B spectrometer using tetramethylsilane as an internal standard.

13) R.L. Shriner and C.N. Wolf, *J. Am. Chem. Soc.*, **73**, 891 (1951).

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

became dark green and gradually disappeared. Three compounds, V (0.08 g), VI (0.20 g), and VIII (trace) were isolated in the same treatment as that described for I. XIX was identified by glc retention time.

Reaction of I with Methylmagnesium Iodide——To an ethereal solution of methylmagnesium iodide prepared from methyl iodide (3.2 g) and Mg (0.6 g), I (1.7 g) was added under nitrogen. A colorless solid was obtained in the customary way. Recrystallization from pet. ether gave 9-methyl-9-phenylxanthene (XIV) as colorless prisms (0.9 g), mp 103°. *Anal.* Calcd. for $C_{20}H_{16}O$: C, 88.18; H, 5.92. Found: C, 88.31; H, 5.94. NMR ($CDCl_3$) τ: 2.6—3.2 (13H, multiplet, aromatic H), 8.1 (3H, singlet, CH_3).

Reaction of I with *o*-Methoxyphenylmagnesium Bromide——*o*-Methoxyphenylmagnesium bromide prepared from *o*-bromoanisole (2.4 g) and Mg (0.4 g) was added to a suspension of I (1.78 g) in ether under nitrogen. The reaction mixture was stirred for 10 hr and treated as mentioned above. Separation of the crude product gave following three compounds. 9-(*o*-Methoxyphenyl)-9-phenylxanthene (XII) $C_{26}H_{20}O_2$: was recrystallized from benzene–pet. ether to give 0.58 g of colorless prisms, mp 157°. *Anal.* Calcd. for C, 85.69; H, 5.53. Found: C, 85.82; H, 5.69. NMR ($CDCl_3$) τ: 2.50—3.50 (17H, multiplet, aromatic H), 6.77 (3H, singlet, OCH_3). V (0.30 g). VIII (trace).

Reaction of I with *p*-Methoxyphenylmagnesium Bromide——*p*-Methoxyphenylmagnesium bromide prepared from *p*-bromoanisole (2.4 g) and Mg (0.4 g) was added to a suspension of I (1.7 g) in ether under nitrogen. The reaction mixture was treated as mentioned above. The products were 9-(*p*-methoxyphenyl)-9- phenylxanthene (XIII) (0.71 g), V (0.26 g), and VIII (trace). XIII was recrystallized from benzene–pet. ether as colorless prisms, mp 190°. *Anal.* Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.63; H, 5.64. NMR ($CDCl_3$) τ: 2.54—3.41 (17H, multiplet, aromatic H), 6.23 (3H, singlet, OCH_3).

Reaction of VIII with Perchloric Acid——To a suspension of VIII (0.2 g) in ether (20 ml) containing a small amount of AcOH, 70% perchloric acid (1 ml) was added, and the reaction mixture was stirred for 1 hr. The resulting yellow precipitate was filtered and washed with ether. Recrystallization from AcOH gave I (0.2 g), mp 280° (decomp.) (reported[13] 280—281° (decomp.)). This compound was identified with the authentic specimen prepared from 9-phenylxanthenol.

9-Phenyl(-*d*$_5$)xanthylium Perchlorate (X)——The procedure was a modification of a literature procedure for I.[4e,13] Xanthone (2 g) was added to an ethereal phenyl(-d_5)magnesium bromide solution prepared from bromobenzene (-d_5) (3 g) and Mg (0.6 g). After refluxing for 8 hr the reaction mixture was worked up in the usual manner. Crude 9-phenyl(-d_5)xanthenol (2 g) which resulted was treated with 70% perchloric acid. The yellow precipitate thus formed was filtered and washed with ether. Recrystallization from AcOH gave yellow plates (2 g), mp 282° (decomp.). *Anal.* Calcd. for $C_{19}H_8O_5D_5Cl$: C, 63.07; H, 5.03. Found: C, 63.07; H, 5.22.

Diphenyl-*o*-phenoxyphenylmethanol (XVI)——A mixture of *o*-chlorobenzophenone (4.3 g), Cu powder (0.5 g), and C_6H_5ONa prepared-from phenol (2 g) and NaOH (1 g) was molten for 1 hr at 160—200°. The cooled reaction mixture was taken up in benzene. Removal of benzene gave crude *o*-phenoxybenzophenone (XV) (4 g). A Grignard reagent prepared from bromobenzene (4.7 g) and Mg (0.7 g) was added to an ethereal solution of XV. After refluxing for 5 hr the reaction mixture was treated in the usual way. The resulting solid was recrystallized from ether–pet. ether to give 4.2 g of colorless prisms, mp 123° (reported[9] 112°). *Anal.* Calcd. for $C_{25}H_{20}O_2$: C, 85.19: H, 5.72. Found: C, 85.26; H, 5.92. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3550 (OH).

***p*-Biphenylyl-*o*-phenoxyphenylmethanol (XVII)**——XV was prepared from phenol (1.4 g), NaOH (0.7 g), and *o*-chlorobenzophenone (3 g) as mentioned above. To a Grignard reagent prepared from 4-bromobiphenyl (4.9 g) and Mg (0.6 g), a benzene solution of XV was added. The reaction mixture was refluxed for 15 hr and worked up in the usual way. The colorless solid which resulted was recrystallized from benzene–pet. ether to give 2 g of colorless prisms, mp 150°. *Anal.* Calcd. for $C_{31}H_{24}O_2$: C, 86.88; H, 5.64. Found: C, 86.83; H, 5.68. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3235 (OH).

9-(*p*-Biphenylyl)-9-phenylxanthene (XVIII)——A solution of XVII (0.4 g) in AcOH (30 ml) added with conc. H_2SO_4 (2 drops) was refluxed for 1 hr. After removal of AcOH the residue was taken up in benzene. Evaporation left colorless crystals. Recrystallization from benzene–pet. ether gave colorless prisms (0.25 g), mp 200—201°. *Anal.* Calcd. for $C_{31}H_{22}O$: C, 90.70; H, 5.40. Found: C, 90.77; H, 5.40.

9-(*o*-Methoxyphenyl)-9-phenylxanthene (XII) and *p*-Isomer (XIII)——XV was prepared from phenol (2 g), NaOH (1 g), and *o*-chlorobenzophenone (4.3 g). To a Grignard reagent prepared from *o*-(or *p*-) bromoanisole (5.4 g) and Mg (0.7 g), a benzene solution of XV was added. The reaction mixture was refluxed for 5 hr and worked up in the usual way. After purification by column chromatography the resulting solid was dissolved in AcOH (50 ml) containing conc. H_2SO_4 (1 ml). The reaction mixture was refluxed for 2 hr and treated as mentioned above. XII was recrystallized from benzene–pet. ether to give 3.5 g of colorless prisms, mp 157°. *Anal.* Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.72; H, 5.64. NMR ($CDCl_3$) τ: 2.50—3.50 (17H, multiplet, aromatic H), 6.77 (3H, singlet, OCH_3). XIII was recrystallized from benzene–pet. ether to give 4.0 g of colorless prisms, mp 189°. *Anal.* Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.78; H, 5.76. NMR ($CDCl_3$) τ: 2.42—3.42 (17H, multiplet, aromatic H), 6.24 (3H, singlet, OCH_3).

9-Phenylxanthene (V)——V was prepared by the reduction of I (0.5 g) with $LiAlH_4$ (0.2 g) in the usual way. Recrystallization from pet. ether gave colorless prisms (0.3 g), mp 147°, (reported[9] 145°).

1-Phenylethanol (XIX)——XIX was prepared by the reduction of acetophenone (5 g) with $NaBH_4$ (1 g) in the customary way. Distillation gave colorless oil (4.5 g), bp 105°/20 mm. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3325 (OH).

Hydrogen Abstraction by IX from Ethyl Ether——A suspension of I (1.00 g) and Zn powder (0.5 g) in THF (35 ml) was stirred for 1.5 hr under nitrogen atmosphere, and then anhydrous ether (35 ml) was added. Stirring was continued for a day, and dry air was passed through the reaction mixture to convert the remaining IX into peroxide VIII. After removal of the solvent, the residue was washed with ether. Evaporation of the ether washings afforded 9-phenylxanthene (V) (0.32 g), mp 147°. An ether-insoluble material was extracted with hot benzene. Removal of the solvent gave VIII (0.45 g).

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