TABLE 3: The Charge Transfer Quantity from Pyrimidine Bases to 8–Methoxypsoralen

Possible photoadduct	8–MOP–4	8–MOP–4	8–MOP–4′	8–MOP–5′
Thy(5, 6)◇(3, 4)Ps Thy(5, 6)◇(4′, 5′)Ps	0.1456	0.0077	0.0256	0.0016
Thy(6, 1)◇(3, 4)Ps Thy(6, 1)◇(4′, 5′)Ps	0.0374	0.03000	0.0066	0.0062
Cyt(5, 6)◇(3, 4)Ps Cyt(5, 6)◇(4′, 5′)Ps	0.1396	0.0010	0.0246	0.0002
Cyt(6, 1)◇(3, 4)Ps Cyt(6, 1)◇(4′, 5′)Ps	0.0048	0.0299	0.0008	0.0061

photosubstitution reaction.[2] In attempt to obtain the more precise information for the photoreactions between furocoumarins and DNA, a solution of a labelled furocoumarin and a native DNA was irradiated under long wavelength uv light.[15] The photoadducts isolated were identical with the photoadducts formed between psoralen and pyrimidine bases[16].

In conclusion, the results of FMO method are in good agreement with the experimental observations in interpreting the regioselectivity of photocycloaddition reactions between psoralens and DNA and can be utilized in predicting the photoreactivities of psoralens to purine and/or pyrimidine bases of DNA.

Acknowledgement. This work has been supported by the National Cancer Institute, DHHS, U. S. A. (Grant No. 5 RO 1 CA 21729) to SCS and by the Korea Science and Engineering Foundation Postdoctoral Fellowship to JHK.

References

(1) W. W. Mantulin and P–S. Song, *J. Amer. Chem. Soc.*, **95**, 5122 (1973).
(2) P–S. Song, M. L. Harter, T. A. Moore and W. C. Herndon, *Photochem. Photobiol.*, **14**, 521 (1971).
(3) P–S. Song and W. H. Gordon, *J. Phys. Chem.*, **74**, 4234 (1970).
(4) T. A. Moore, M. L. Harter and P–S. Song, *J Mol. Spect.*, **40**, 144, (1971).
(5) J. H. Kim and S. C. Shim, *Bull Korean Chem. Soc.*, **1**, 71 (1980).
(6) J. H. Kim, Ph. D. Dissertation, Chonnam National Univ., p. 50–55, 1980.
(7) D. Elad "Photochemistry and Photobiology of Nucleic Acids", Edited by S. Y. Wang, Academic Press, N. Y., 1976. p. 357–380,
(8) C. N. Ou and P–S. Song, *Biochem.*, **17**, 1054 (1978).
(9) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **27**, 1247 (1957).
(10) G. Klopman, "Chemical Reactivity and Reaction Paths", p. 23–50, John Wiley & Sons, N.Y., 1974.
(11) B. Pullman and A. Pullman, "Quantum Biochemistry", p. 107–110, Interscience, N. Y., 1963.
(12) L. Musajo and F. Bordin, *Photochem. Photobiol.*, **6**, 711 (1967).
(13) L. Musajo, F. Bordin, and R. Bevilacqua, *Photochem. Photobiol.*, **6**, 927 (1967).
(14) C. H. Krauch, D. M. Kramer and A. Wacker, *Photochem. Photobiol.*, **6**, 341 (1967).
(15) L. Musajo, G. Rodighiero, A. Breccia, F. Dall'Acqua and G. Malesani, *Photochem. Photobiol.*, **5**, 739 (1966).
(16) F. Bordin, L. Musajo and R. Bevilacqua, *Z. Naturforsh(B)*, **24**, 691 (1969).

Reactions of Thioxanthylium Ion with Organomercurials

Dong Myung Shin and Kyongtae Kim†

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151, Korea

(Received June 12, 1981)

Reactions of thioxanthylium ion with dimethyl–, dibenzyl–, diisopropyl–, and diphenylmercury in the air gave 9,9′–methylenedithioxanthene, 9–benzylthioxanthene, 9–acetonylthioxanthene, and 9–phenylthioxanthene, respectively, as a 9–substituted thioxanthene. In contrast with reactions with aromatics with an electron–donating group, large amount of thioxanthene and thioxanthone were obtained. However, only trace amounts of thioxanthene and thioxanthone were obtained from the reaction with dibenzylmercury under nitrogen atmosphere. In order to explain these reactions, one electron transfer between thioxanthylium ion and organomercurials was proposed.

Indroduction

Thioxanthylium ion has been prepared by adding either thioxanthene or thioxanthene 10–oxide in 96% sulfuric acid and identified clearly by the spectroscopic methods.[1] The products obtained from the sulfuric acid solution containing thioxanthene were thioxanthone and thioxanthenesulfonic acid, whereas the products obtained from the thioxanthene 10-oxide in sulfuric acid were thioxanthene and thioxanthone. Oxidative scission of bithioxanthyl in 96% sulfuric acid gave also thioxanthylium ion.

The isolation of thioxanthylium ion as a stable salt was achieved in 94 % yield by the oxidative scission of bithioxanthyl with bromine in carbon tetrachloride.[1] Price and co-worker[2] prepared thioxanthylium perchlorate in 61% yield from the reaction of thioxanthen-9-ol with 70% perchloric acid. They synthesized 9-phenylthioxanthene in 83% yield and 9-methylthioxanthene in 80 % yield by the reactions with phenylmagnesium bromide and methylmagnesium iodide, respectively. In contrast, 10-phenyl-10-thianthracene was obtained in 37.5% yield from the reaction with phenyllithium. The mechanism of the formation of the products was proposed to follow the electrophilic substitution of organometallics by thioxanthylium ion. However, the formation of bithioxanthyl with a yield of 14% from the reaction with phenyllithium[2] indicated that a radical mechanism was involved in this reaction to a considerable degree besides the ionic mechanism.

Subsequent studies[3] revealed that bithioxanthyl was indeed formed from the dimerization of thioxanthyl radical. Furthermore, Hori and co-workers[4] examined more thoroughly the possible intervention by radical mechanism in this reaction by the investigation of the reaction between 9-phenylthioxanthyl radical and Grignard reagents or phenyllithium in the presence and absence of $CoBr_2$ which caused a radical reaction of Grignard reagents. Their results showed that 9-phenylthioxanthyl radical reacted with only methylmagnesium iodide and phenyllithium in the presence of $CoBr_2$ to give 9-methyl-10-thioanthracene, respectively. No 9,9-diphenylthioxanthene was obtained from the reaction with phenylmagnesium bromide in the presence of $CoBr_2$.

The failure for the formation of 9,9-diphenylthioxanthene suggests that the compound obtained from 9-thioxanthylium perchlorate with phenylmagnesium bromide is formed by the ionic mechanism. There is no explanation about the reason for the reactivity difference of methylmagnesium iodide and phenylmagnesium bromide toward 9-phenylthioxanthyl radical.

The preparation of thioxanthylium perchlorate was achieved by the reaction of thioxanthene with thianthrene cation radical perchlorate.[5] The ready reduction of the thianthrene cation radical to thianthrene leaded to the formation of thioxanthrene cation radical, which then rapidly transformed to the thioxanthylium ion. By addition of a variety of aromatic compounds bearing an electron-donating group to the thioxanthylium ion in situ was obtained a corresponding 9-substituted thioxanthene.

In order to understand further the reaction of thioxanthylium ion with organometallics, the reactions of thioxanthylium ion with organomercurials were undertaken.

We wish to report here some studies on the reactions between thioxanthylium ion and dimethyl-, dibenzyl-, diisopropryl-, and diphenylmercury.

Experimental

Materials

Thianthrene (Merck) and thioxanthene (Pfaltz and Bauer) were used without further purification. Dimethylmercury, diphenylmercury, and dibenzymercury were obtained from Eastman Kodak, ICN K & K laboratory Inc., and Alfa Products, respectively. Acetonitrile was Kanto Chemical Corporation Extra pure and was refluxed with phosphorus pentoxide for 3 hr, followed by distilling twice. Dried acetonitrile was stored over molecular sieve (4 Å) in a septum-capped bottle. Acetic anhydride and carbon tetrachloride were Kanto Chemical Corporation Extra pure and redistilled before use. Perchloric acid (70%) was Wako pure Chemical Industry Ltd. extra pure. All solvents were EP grade unless otherwise specified and distilled before use.

Thin layer chromatography was carried out with Merck, Kiesel gel 60, PF 254 and the chromatogram was visualized by mineral ultraviolet lamp.

Column chromatography was performed with Merck, Kiesel gel 60, 70-230 *ASTM* mesh, 0.0200-0.063 mm (Cat. No. 7734). Eluant solvents are specified in each case.

Ultraviolet spectra were obtained using Hitachi 124 and Beckman Model 5720 UV-VIS spectrophotometers. Infrared spectra were obtained with Jasco Model IR-G and Perkin-Elmer Model 283 infrared spectrophotometers. All infrared spectra were taken using potassium bromide pellets.

^1H nmr spectra were recorded with Varian EM 360A spectrometer and the data were given in δ units downfield from tetramethylsilane.

Melting points are uncorrected. Mercury analysis was performed by Korea Research Institute of Chemical Technology. Mass spectra were obtained from College of Pharmacy, SNU.

Experiments

Thianthrene cation radical perchlorate was prepared by by the method of Rundel and Schffer.[6]

Reaction with Dimethylmercury. Thianthrene cation radical perchlorate (742 mg, 2.35 mmol) was placed in 100 m*l* round bottomed flask. After 20 m*l* of dry acetonitrile was added, the flask was stoppered. The mixture was stirred for 10 min, followed by rapid addition of 243 mg (1.23 mmol) of thioxanthene. Dark purple color of the cation radical solution turned immediately dark red, which was stirred for an additional 25 min. To this was added rapidly 0.54 m*l* (1721 mg, 7.46 mmol) of dimethyl mercury using a pipet. The color of the solution turned immediately violet, followed by dark red in 10 min-strirring. The reaction mixture was stirred continuously for an additional 10 min but no further color change was observed. After 20 hr, the solution became again violet and thin layer chromatography performed on the silica gel plate with a mixture of hexane (300 m*l*) and ether (1 drop) showed three spots, indicating thianthrene, thioxanthene, thioxanthone, and two unknown spots near and at the original spot. The solvent of the reaction mixture was removed using a rotary evaporator and the residue was chromatographed on silica gel (Wako gel Q-12, 28–200 mesh, 5.5×2.5 cm) column. No compound was obtained in the first 160 m*l* of hexane. A white solid (601 mg) was obtained from the next eleven fractions (800 m*l*), which showed ultraviolet absorptions at 256, and 240 nm. ^{1}H nmr ($CDCl_3$) spectrum of the white solid exhibited a singlet at δ4.14 ppm and a multiplet around δ7 ppm. The integrated ^{1}H nmr spectrum indicated that the white compound consisted of 506 mg (2.34 mmol) of thianthrene and 95 mg (0.48 mmol) of thioxanthene. Elution (160 m*l*) with a mixture of hexane (300 m*l*) and ether (15 drops) gave 103 mg of yellowish white solid, exhibiting absorption maxima at 256, 240, and 211 nm. Tlc [hexane (300 m*l*)–ether (1 drop) as an eluant] showed two spots in addition to two spots corresponding to thianthrene (or thioxanthene) and thioxanthone.

So the solid was rechromatographed on silica gel column (1.2×6 cm).

Elution (70 m*l*) with a mixture of hexane (300 m*l*) and ether (1 drop) gave 50 mg of a white solid, consisting of 24 mg of thianthrene and 26 mg of thioxanthene and subsequent 40 m*l* of eluant gave 45 mg of a white solid, exhibiting brown fluorescence by illumination with a mineral UV lamp. R_f value of this spot was smaller than that of thioxanthone. The compound was recrystallized from EtOH–acetone (10:1, v/v), m. p, 184–185 °C. Decolorization, followed by recrystallization from ethanol–acetone (10:1, v/v) gave a white powder, m.p, 184–185 °C. UV: λ_{max}^{EtOH} 268, 217 nm, ^{1}H nmr ($CDCl_3$) δ2.20 (*t*, 2H, methylene, J=3.8 Hz), 3.84(*t*, 2H, 2methine, J=3.8 Hz), and 7.27 (*m*, 16H, aromatic) ppm. This compound was assigned to be 9,9′–methylenedithioxanthene. Elution(180 m*l*) with hexane (300 m*l*)–ether (30 drops), followed by benzene (30 m*l*) gave 28 mg of residue, consisting of 4 mg of thianthrene, 2 mg of thioxanthene, 16 mg of thioxanthone, and 9 mg of 9,9′–methylenedithioxanthene.

Elution with benzene (130 m*l*) continuously, followed by 120 m*l* of a mixture of benzene (300 m*l*) and acetone (20 drops) gave 94 mg and 14 mg of yellow residue, respectively after removal of the solvent. Tlc [hexane (300 m*l*)–ether (1 drop) as a solvent] of the benzene fraction showed 3 spots whose R_f values was identical with those of thianthrene or thioxanthene and thioxanthone, respectively. Analysis of ^{1}H nmr spectrum of the residue obtained from benzene fraction indicated that the mixture consisted of 11 mg of thianthrene and 78 mg of thioxanthone, and 5 mg of thioxanthene.

Elution with acetone gave 637 mg of purple, sticky residue, having UV absorptions at 266 and 220 nm in ethanol. Purification of the sticky residue has been tried in several ways. The residue was dissolved in $CDCl_3$ to take ^{1}H nmr spectrum but some white solid remained in the tube. ^{1}H nmr spectrum was not good. In order to get more solid was added 15 m*l* of chloroform to the residue. However, the solid disappeared and the solution became violet. No solid was formed by the concentration of the solvent up to 4 m*l*. Upon addition of 5 m*l* of methanol to chloroform solution, solution became colorless. Again upon concentration of the solution, color of the solution returned to violet. The violet residue was dissolved in acetone and then addition of small amount of methanol to the acetone solution caused the solution yellow. The solution was extracted with 15 m*l* of hexane five times. The combined hexane layer was violet and acetone–methanol layer was pale red. However, both fractions seemed to consist of the same components in view of two spots on tlc plate (ethanol as a solvent) in spite of different color. The acetone–methanol layer was evaporated to dryness and the sticky, oily material was washed with 10 m*l* of chloroform three times. The residue was dried under vacuum but it remained oily, stinking material, which did not turn solid even in dry ice–acetone temperature.

The rest of the residue obtained from the acetone fraction was washed with hexane containing small amount of acetone. The hexane–acetone soluble material was chromatographed on silica gel column (0.9×6 cm). Elution with benzene (25 m*l*) gave a white solid, exhibiting three spots on tlc plate [hexane (300 m*l*)–ether (1 drop)]. Two of these spots had the same R_f values of thianthrene or thioxanthene and thioxanthone, respectively. Elution with ether (10 m*l*) did not give any residue. Finally, acetone fraction (10 m*l*) showed a strong spot at the origin with very weak two spots corresponding thianthrene or thioxanthene and thioxanthone in ethanol as a solvent. The residue (69 mg) was recrystallized from chloroform, m.p, 110–112 °C, ^{1}H nmr ($CDCl_3$–Acetone–d_6) δ1.1 (*s*, methyl) ppm. IR (KBr): 1395, 1100 (perchlorate), 3350 (OH stretch), and 1620 (OH bend) cm^{-1}. This data was consistent with those expected from methylmercury perchlorate. Infrared absorptions at 3350 and 1620 cm^{-1} are thought to be due to the hygroscopic nature of methylmercury perchlorate.

Reaction with Dibenzylmercury

In the Air. To the solution of 788 mg (2.50 mmol) of thianthrene cation radical perchlorate in 20 m*l* of dry acetonitrile was added 261 mg (1.32 mmol) of thioxanthene. After the mixture was stirred for 20 min, 1053 mg (2.75 mmol) of dibenzylmercury was rapidly added. The dark color of the solution turned pale yellow in 20 min and much white solid remained. The reaction mixture was continuously stirred for 16 hr and mercury formed during that time was identified with the naked eye. After the solvent was removed using a rotary evaporator, the residue was chromatographed on silica gel (2.5×9 cm) column. The first hexane fraction (160 m*l*) had no residue. The second hexane fraction (210 m*l*) gave 188 mg of a white residue which showed a spot on tlc plate [a mixture of hexane (150 m*l*)–ether (1 drop) as a solvent]. Crude m.p was 124–143 °C. Ultrviolet spectrum (EtOH) showed maximum absorptions at 256 and 240 nm. ^{1}H nmr spectrum ($CDCl_3$) showed a doublet at δ2.98 (benzylic H), a singlet at δ3.80 (methylene H), a triplet at δ4.18 (methine H), and a mutiplet at δ7.22 ppm. In spite of one spot on tlc plate this fraction consisted of thianthrene, thioxanthene, and 9-benzylthioxanthene in the ratio of 12.9:1:1.4.

Elution continuously with hexane (520 m*l*) gave 206 mg of a white residue, showing two spots on tlc plate in the same solvent as in the previous fraction.

Rechromatography on silica gel (2.5×6.5 cm), using the mixture of hexane (150 m*l*)-ether (1 drop) followed by the recrystallization from ethanol gave a 185 mg of a needle-type crystal, identified as 9-benzylthioxanthene, m.p, 132–134 °C. ^1H nmr spectrum ($CDCl_3$) δ2.99 (*d*, 2H, benzylic, J=4 Hz), 4.17 (*t*, 1H, methine, J=3.5 Hz), and 7.13 (*m*, 13H, aromatic). IR (KBr): 3120, 3070, 2980, 2920, 1496, 1470, 1440, 1268, 1080, 1070, 1039 cm^{-1}. UV λ_{max}^{EtOH} 268, 250 (shoulder), 228 (shoulder), and 216 nm. Benzene was used as a next solvent. The first benzene fraction (15 m*l*) consisted of 26 mg of thianthrene, 34 mg of thioxanthene, and 26 mg of 9-benzylthioxanthene. The second benzene fraction (50 m*l*) gave 211 mg of residue consisting of 50 mg of thianthrene, 40 mg of thioxanthene, 50 mg of 9-benzylthioxanthene, and 60 mg of thioxanthone. Elution next with ether (90 m*l*) gave 131 mg of residue, consisting of 121 mg of thianthrene and 10 mg of thioxanthone. ^1H nmr ($CDCl_3$) of the residue exhibited two multiplets centered at δ8.02 and 7.25 ppm which corresponded to two protons of 1 and 8 positions of thioxanthone and aromatic protons of thioxanthone and thianthrene, respectively. The ratio of two peaks indicated the relative amount of the two compounds in the mixture.

The final elution was carried out with acetone in which three fractions (30, 60, 160 m*l*) were collected. The first acetone fraction gave 587 mg of residue which recrystallized from ethanol, giving 62 mg of pale yellow crystal, m.p, 146–156 °C. Ultraviolet spectrum of the crystal exhibited an absorption at 256 nm. ^1H nmr ($CDCl_3$) showed a multiplet between 7 and 8 ppm which was exactly identical with that of thianthrene. Aside from ethanol soluble material, 103 mg of ethanol insoluble material was filtered and it decomposed in the range of 225 and 237 °C. No UV absorption was obatained from this compound. ^1H nmr (DMSO-d_6) showed absorptions in the region of aromatic protons. No further identification was attempted.

The second acetone fraction gave 331 mg of residue which was recrystallized from ethanol to give 63 mg, m.p, 145–157 °C. UV λ_{max}^{EtOH} 256 and 240 nm. From this fraction was obtained 28 mg of ethanol insoluble material. The third acetone fraction gave 108 mg of residue of which ethanol soluble and insoluble materials were 98 mg and 10 mg, respectively.

Under N_2 Atmosphere. To the solution of 1371 mg (4.35 mmol) of thianthrene cation radical perchlorate in 20 m*l* dried acetonitrile was added 445 mg (2.25 mmol) by thioxanthene. Nitrogen was bubbled through the reaction mixture, followed by the addition of 1678 mg (4.35 mmol) of dibenzylmercury. The mixture was stirred for 19 hr and then chromatographed as in the previous reaction (2.5×10 cm).

Elution with hexane (250 m*l*) gave 538 mg of 9-benzylthioxanthene.

Elution next with benzene (80 m*l*) gave 50 mg of thianthrene, 21 mg of 9-benzylthioxanthene, and a trace amount of unknown compound.

Elution with ether (70 m*l*), followed by acetone (50 m*l*) gave 253 mg and 859 mg of brown residue, respectively. These residues were rechromatographed on the silica gel (2.5×8 cm) column. Elution with benzene (105 m*l*) gave 246 mg of thianthrene and 9 mg of thioxanthene.

Elution with ether (60 m*l*) gave 213 mg of thianthrene 5-oxide, identified by the characteristic its ir band of S=O at 1170, 1110, and 1070 cm^{-1}.

Elution with acetone (80 m*l*) gave 430 mg of unknown brown solids whose structural identification has been unsuccessful. In the meantime, acetone fraction of the first chromatography gave 1331 mg of yellow solid which was extracted with chloroform (40 m*l*) to give 569 mg of chloroform soluble material and 255 mg of insoluble material in chloroform. Recrystallization of the former from ethanol afforded 451 mg of thianthrene, m.p, 157–158 °C.

The latter was insoluble in common organic solvents and decomposed at 255–260 °C. IR (KBr): 3500, 1600, 1430, 1250, 1100, 760, and 620 cm^{-1}. It was unsuccessful to record good ^1H nmr spectrum.

Reaction with Diisopropylmercury

Treatment of the Reaction Mixture with Acetone. To the stirred solution of 1678 mg (5.33 mmol) of thianthrene cation radical perchlorate in 20 m*l* of dry acetonitrile was added 558 mg (2.82 mmol) of thioxanthene. After the color of the cation radical had disappeared, diisopropylmercury (1 m*l*, 2003 mg, 6.83 mmol) was added to the dark red reaction mixture. The color of the solution turned immediately purple. After the reaction mixture was stirred for 110 hr the solvent was removed under vacuum. To the dried reaction mixture was added 30 m*l* of acetone-acetonitrile (1:9, v/v), followed by addition of some silica gel in order to adsorb all the reaction mixture into the silica gel. Again the solvent was removed under vacuum and then the mixture was transferred to the column (2.5× 13 cm).

Elution with 340 m*l* of a mixture of hexane (300 m*l*) and ether (1 drop) gave 1155 mg (5.34 mmol) of thianthrene, 294 mg (1.48 mmol) of thioxanthene, and 145 mg of unidentified yellowish solids, which showed no ultraviolet absorption in methanol. Next fraction (35 m*l*) gave 173 mg (0.82 mmol) of thioxanthone. Elution with benzene (50 m*l*) afforded 121 mg of yellolish solid, which was recrystallized from methanol. m.p, 69–70 °C. UV $\lambda_{max}^{Methanol}$ 266 nm. ^1H nmr ($CDCl_3$): δ : 1.96 (*s*, 3H,methyl), 2.90 (*d*, 2H, methylene, J=7.2 Hz), 4.69 (*t*, 1H, methine, J=6.9 Hz), 7.0–7.6 (*m*, 9H, aromatic) ppm. IR (KRr): 3050, 3000, 2925, 1710, 1580, 1560, 1465, 1440, 1350, 1290, 1270, 1250, 1150, 1110, 1060, 1030 750 cm^{-1}.

This compound was identified as 9-acetonylthioxanthene. *No treatment of the Reaction Mixture with Acetone.* To the stirred solution of 883 mg (2.80 mmol) of thianthrene cation radical perchlorate in 20 m*l* of dried acetonitrile was added 301 mg (1.52 mmol) of thioxanthene. After the color of cation radical had disappeared, diisopropylmercury (0.4 m*l*, 800 mg, 2.79 mmol) was added to the dark red reaction mixture. This reaction mixture was treated as in the previous reaction except that no acetone was used in the process of transferring the reaction mixture into the column. From this reaction was obtained 603 mg (2.79 mmol) of thianthrene, 87 mg (0.44 mmol) of thioxanthene, and 25 mg (0.10 mmol) of 9-acetonylthioxanthene.

Reaction with Acetone. To the stirred solution of 1680 mg (5.36 mmol) of thianthrene cation radical perchlorate in 20 m*l* of dried acetonitrile was added 553 mg (2.79 mmol) of thioxanthene. After color of the cation radical had disappeared, dried acetone (0.4 m*l*, 315 mg, 5.43 mmol) was added to the reaction mixture. The reaction mixture was stirred for 4 min and then the solution became red.

This reaction mixture was stirred for 21 hr, followed by column chromatography on the silica gel (2.5×7 cm).

Elution with benzene (350 m*l*) gave 1208 mg (5.59 mmol) of thianthrene, 102 mg (0.52 mmol) of thioxanthene, and 135 mg (0.53 mmol) of 9-acetonylthioxanthene.

Reaction with Diphenylmercury

To the solution of 813 mg (2.58 mmol) of thianthrene cation radical perchlorate in 20 m*l* of dry acetonitrile was added 355 mg (1.79 mmol) of thioxanthene. The mixture was stirred for 10 min and then 1000 mg (2.82 mmol) of diphenylmercury was rapidly added to the dark red solution. The reaction mixture was continuously stirred for 60 hr at room temperature and the solution became yellow. After the solvent was evaporated to dryness using a rotary evaporator, the residue was chromatographed on a silica gel (Wakogel Q-12, 28-200 mesh, 2.5×15 cm) column.

Elution with hexane (100 m*l*×10) gave 677 mg of a mixture, consisting of 510 mg of thianthrene and 167 mg of thioxanthene.

Elution next with benzene (15 m*l*) gave 122 mg of yellow solid which was recrystallized from ethanol twice to give white crystal, m.p, 95 °C (*lit*[5]. 96 °C). UV λ_{max}^{EtOH} 267 and 209 nm. IR (KBr): 3055, 1580, 1485, 1460, 1442, 730, and 690 cm^{-1}. ^{1}H nmr ($CDCl_3$) δ5.33 (s, 1H, methine), 7.1–7.4 (*m*, 13H, aromatic) ppm. This compound was identified as 9-phenylthioxanthene.

Elution with benzene (320 m*l*) continuously gave 25 mg of thioxanthene, 104 mg of thioxanthone, and 112 mg of 9-phenylthioxanthene.

Elution next with a mixture of ether and ethyl acetate (9:1, v/v, 200 m*l*) gave 229 mg of red residue which showed five spots on tlc plate (hexane).

Rechromatography (Wako gel, 28–200 mesh, 2.5×8 cm) of the red residue with benzene gave 4 mg of solid, still showing two spots on tlc plate (hexane), whose R_f values were not consistent with that of either thianthrene or thioxanthene. It was unsuccessful to separate the rest of materials.

Elution with ethyl acetate (100 m*l*) gave 288 mg of red residue, showing several spots on tlc plate (benzene). In order to separate a major component the residue was rechromatographed on the silica gel (Wako gel Q-12, 28–200 mesh, 2.5×10 cm) column using a series of eluants such as benzene (100 m*l*), ether (30 m*l*), ether–acetone (3:1, v/v, 30 m*l*), ether–acetone (1:5, v/v, 30 m*l*), and methanol (30 m*l*). Of these fractions, ether–acetone (1:5, v/v) fraction gave 164 mg of red residue but only minute amount of residue was obtained from the other fractions. The red residue showed a major spot at the origin, along with two very weak spots near the solvent line (benzene as an eluant).

Recrystallization of the red residue from methanol gave pale red crystal which decomposed to brown material at 95 °C. ^{1}H nmr spectrum (acetone-d_6–$CDCl_3$) of the pale red crystal exhibited a broad singlet at δ4.95 ppm and a multiplet centered at δ7.33 ppm. The singlet peak was believed to be due to water because it became bigger by adding a drop of water.

Major peaks of IR (KBr): 3466, 1422, 1131, 1117, 676, and 613 (ClO_4) cm^{-1}.

UV λ_{max}^{EtOH} 216 nm. All spectroscopic data was consistent with those expected from phenylmercury perchlorate. The compound was analyzed by atomic absorption spectrometer and found to contain mercury in it although there was difference between experimental (64.1%) and theoretical (53.9%) values.

Elution with acetone (50 m*l*) gave 360 mg of a mixture of red and white residue which was rechromatographed on a silica gel (Wako gel Q-12, 28–200 mesh, 1.8×12 cm) column using hexane-benzene (95:5, v/v), benzene, benzene–ether (9:1, v/v), and benzene–ether–ethanol (10:10:1, v/v). From the last fraction was obtained 22 mg of red, sticky material, showing absorption maxima at 269 and 220 nm in ethanol and three spots on tlc plate (benzene as an eluant). The red liquid turned slowly brown liquid either in the air or by keeping it over P_2O_5 in the vacuum desiccator. Purification of this material has been unsuccessful.

Results

Reaction of thianthrene cation radical perchlorate with thioxanthene leaded immediately to the dark solution containing much solid. Organomercurials was then added to this reaction mixture. The gradual fade of the color indicated the progress of the reaction.

All of reactions except for the reaction with dibenzylmercury were carried out in the air since in the beginning of this research it was thought that no radical was involved through the reactions.

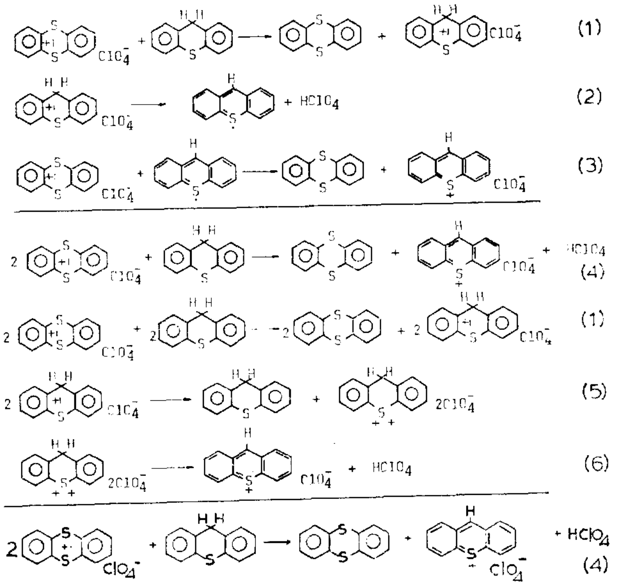
It was rather difficult to separate a mixture of thianthrene and thioxanthene either on silica gel column or by thin layer chromatography using silica gel. However, the mixture exhibited a singlet of methylene proton of thioxanthene at δ4.14 ppm and multiplets in the region of aromatic protons. The composition of two compounds was analyzed by the integration of ^{1}H nmr spectrum.

Reactions with diphenyl- and dibenzylmercury afforded 9-phenyl- and 9-benzylthioxanthene, respectively. The yield of 9-benzylthioxanthene increased markedly under nitrogen atmosphere at the expense of that of thioxanthone. In the case of the reaction of diisopropylmercury, 9-

TABLE 1: Summary of the Reactions of Thioxanthylium Ion and Some Organomercurials

	Reactants (mmol)			Products (mmol)					
	R_2Hg	Th$^{+\cdot}$[a]	Tx[b]	Th[c]	Tx	Tx–R[d]	TxO[e]	$RHgClO_4$	Yield of Tx-R(%)[f]
Mg_2Hg	7.46	2.35	1.23	2.52	0.64(0.06)	0.13	0.44	0.22	22.1
$(C_6H_5CH_2)_2Hg$	2.75	2.50	1.32	2.68	0.43(0.07)	0.79	0.32		63.2
$(C_6H_5CH_2)_2Hg$	4.35	4.35	2.25	3.46	0.04(0.04)	1.95	trace		89.9
i–Pr_2Hg	6.83	5.33	2.82	5.34	2.45(0.16)	0.48			25.9
i–Pr_2Hg[h]	2.79	2.80	1.52	2.79	1.44(0.12)	0.10			7.1
$(C_6H_5)_2Hg$	2.82	2.58	1.79	2.36	0.97(0.50)	0.85	0.49	2.33	66.1
$(CH_3)_2CO$	5.43	5.36	2.79	5.58	0.52(0.61)	0.53			19.8

[a] Thianthrene cation radical perchlorate, [b]thioxanthene, [c]thianthrene, [d]9–substituted thioxanthene, [e]thioxanthone, [f]$\frac{\text{mol of Tx–R}(100)}{1/2\ \text{mol of}\,\text{Th}^{+\cdot}}$ [g]under N_2 atmosphere. [h] Reaction mixture was not treated with acetone before chromatography. [i] No. of moles of excess thioxanthene=No. of moles of Tx(reactant)–1/2 moles of Th$^{+\cdot}$. Tx(product) means all recovered thioxanthenes.



Scheme 1.

isopropylthioxanthene was not obtained. Instead, 9-acetonylthioxanthene was the only identified product. Direct addition of dried acetone to the thioxanthylium ion afforded the identical product. It was not our purpose to find the optimum condition to get high yield of 9–acetonylthioxanthene. This matter is now in progress. All products were identified by the spectroscopic techniques (ir, uv, ^{1}H nmr, mass spectrum) and elemental analyses. The stoichiometric relationships of these reactions are tabulated in the Table 1.

Discussion

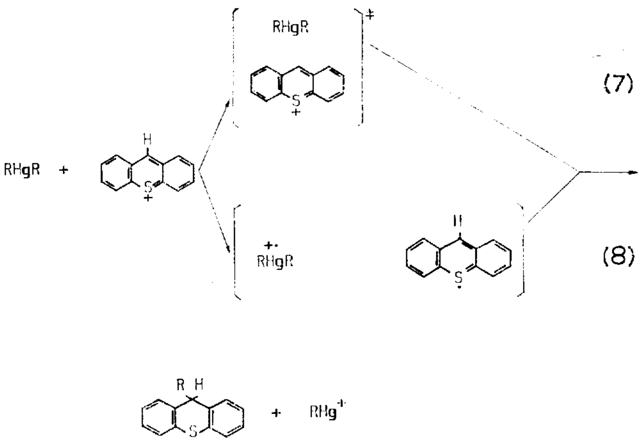
In the previous paper[5], we have proposed the formation of thioxanthylium ion from the reaction of thianthrene cation radical with thioxanthene as shown in Scheme 1.

We do not know yet whether thioxanthene cation radical lose a proton to give a radical species as shown in the eq. (2) or undergoes a disproportionation reaction to give thioxanthene dication which then loses a proton to give thioxanthylium ion as shown in eqs. (5) and (6). In any case, two moles of cation radical reacted with one mole of thioxanthene to produce one mole of thianthren, which was confirmed by the reaction with aromatics with an electron-donating group and one mole of thioxanthylium ion.

Reactions with organomercurials such as dimethyl–, diisopropyl–, diphenyl–, and dibenzylmercury, however, have shown different aspects compared with the reactions with aromatics. In cases of reactions with aromatics, only excess amount of thioxanthene was recovered after work-up procedure. This means that all thioxanthenes react with thianthrene cation radical according to the stoichiometry represented by eq. (4) and thus formed thioxanthylium ion further reacts with aromatics. In contrast, considerable amount of thioxanthene in addition to excess thioxanthene was recovered from the reaction with organomercurials as shown in Table 1.

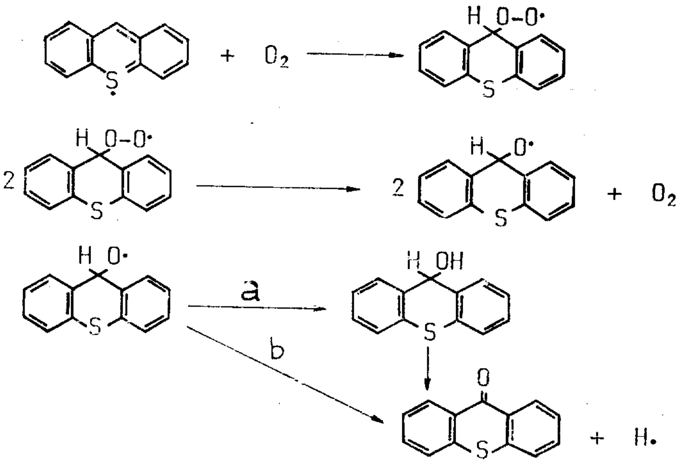
In a majority of the reactions with organomercurials, the cleavage of the carbon–mercury bond proceeds *via* an electrophilic mechanism[7–9]. However, a variety of electrophilic processes have recently been shown to involve prior electron transfer. Kochi[10] has studied that the reaction of dialkyl mercurials with some electrophiles and found the reaction proceed by electron transfer. In particular, the hexachloroididate (IV) ion undergoes rate–determining electron transfer with a series of dialkyl mercurials. The dialkyl mercurial cation radical is formed and given an alkyl radical which is rapidly trapped in the product forming step. Analogously, two mechanisms, namely, electrophilic displacement and electron–transfer as the first step can be applied for the illustration of the reactions of thioxanthylium ion with organomercurials. The mechanistic distinction between electrophilic cleavege of carbon–mercury bond in the reaction of thioxanthylium ion and organomercurials and the reaction proceeding via electron transfer is outlined in eq. (7) and (8), respectively, of Scheme 2.

The nature of the transition state of each pathway is uncertain. However, the fact that aromatics carrying an electron–withdrawing group did not undergo the reaction with the cation indicated that thioxanthylium ion rather than thioxanthene radical as an electron deficient speices reacted with aromatics having sufficient electron density. In such reactions all thioxanthylium ions transformed to either 9–arylsubstituted thioxanthene or unidentified products which showed perchlorate band in their infrared spectra and only thioxanthene added originally beyond the quantitative

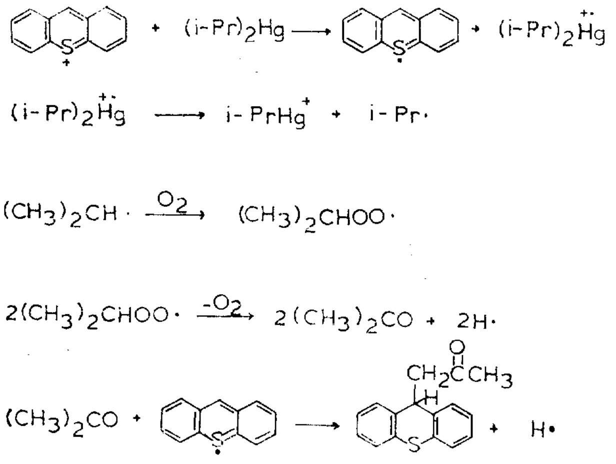


Scheme 2.

amount estimated from eq. (4) was recovered. Therefore, more recovery of thioxanthene from the reactions with dimethyl-, diisopropyl-, diphenyl-, and dibenzylmercury (than that expected from the basis of the above statement) implies that other mechanism may be involved in these reactions. Electron-transfer mechanism as outlined in eq. (8) may be a possible candidate. The eq (8) shows the formation of mercurial cation radical and thioxanthene radical. The former decomposes to give RHg^+ species and R radical. The latter undergoes a coupling reaction with R(R=phenyl, benzyl) radical to give 9-phenyl- and 9-benzylthioxanthene, respectively. Isolation of methylmercuric perchlorate and phenylmercuric perchlorate supports the suggestions in which the decomposition of diphenylmercury cation radical and dibenzylmerucry cation radical to the corresponding mercuric salt occurs. The formation of thioxanthene radical was demonstrated by price and co-worker[2] who obtained corresponding thiopyrylium ion from the reaction of thiabenzene, thianaphthalene and thioxanthene. As a result of the subsequent reaction of the thiopyrylium ion with phenyllithium they observed esr signals and obtained bithioxanthyl, which was believed to be formed by dimerization of thioxanthene radical.

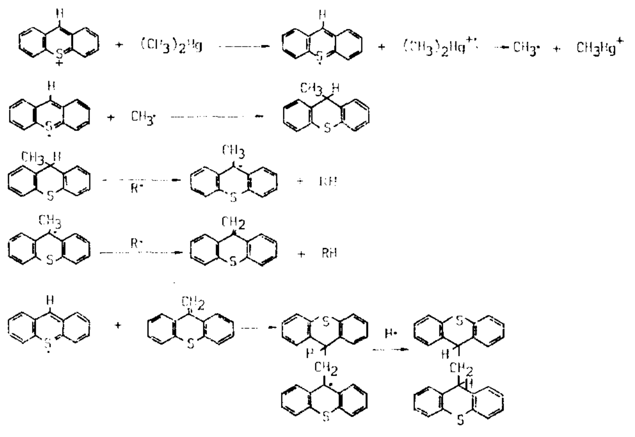


Scheme 3.



Scheme 4.

Other evidence for the involvement of radical mechanism in these reactions is given by the yield of thioxanthone. Thioxanthone can be readily formed by the reaction of thioxanthylium ion with water. Since thioxanthen-9-ol first formed is very unstable in the acidic medium, it is readily oxidized to form thioxanthone. Assuming that the formation of thioxanthone is due to the reaction with water, very small amount of thioxanthone is expected in these reactions because of prior removal of water present in even dry acetonitrile by the reaction with thianthrene cation radical. Indeed, no thioxanthone was isolated from the reactions with aromatics such as anisole, aniline, N,N-diethylaniline, *etc*, except for ethylbenzene whose reaction was very slow. Since the trend of changing color of thioxanthylium indicates the rate of the reaction, it is expected that the reaction maintaining the color of thioxanthylium longer may have more chance to interact with moisture than the reaction changing the color fast. Consequently, the longer reaction time, the more thioxanthone is produced. Reactions with dimethyl-, dibenzyl-, and diphenylmercury were faster reactions than that with anisole. Nontherless, large amount of thioxanthone was isolated form these reactions in the air. The remarkable difference with respect to the yield of thioxanthone between reactions with dimethyl-, dibenzyl-, and diphenylmercury and reactions with aromatics at the similar condition, along with the formation of essentially no detectable amount of thioxanthone in the reaction with dibenzylmercury under nitrogen atmosphere, may support the mechanism proceeding *via* electron transfer in the reactions with organomercurials. The formation of thioxanthone can be depicted in Scheme 3. Analogous reaction mechanism can be obtained from Kochi's results in which Kochi has trapped isopropyl radical from the reaction of diisopropylmercury with hexachloroiridate using spin-trapping technique and isolated acetone as well as iospropyl alcohol as isopropyl radical-oxygen reaction products. The formation of thioxanthone is likely followed by the path (b) on the basis of the comparison between the yield of thioxanthene and thioxanthone. If thioxanthene radical abstracts hydrogen atom from thioxanthene oxy radical, then equimolar amount of thioxanthene and thioxanthone must be formed. Table 1 shows very close relation ship between two compounds except for the reaction of diisopropylmercury which proceeds with essentially the same way as in the other reaction but gives different products as shown in Scheme 4.



Scheme 5.

The failure of isolation of thioxanthone indicates that oxygen is more sensitive to scavenge the isoproprpyl radical than thioxanthene radical. We have not attempted to identify isopropyl alcohol which might be formed by the disproportionation reaction of isopropyl radical. 9-Acetonylthioxanthene could be obtained by the direct addition of acetone to thioxanthylium ion.

In this case the reaction seemed to proceed with an ionic mechanism rather than the radical mechanism. The reaction with dimethylmercury did not give 9-methylthioxanthene. Instead, 9,9′-methylenedithioxanthene was obtained. The reason for this abnormality is presumably due to less steric hindrance of methyl group. Investigation of this possibility using diethylmercury and *bis*-trichloromethylmercury is undertaken. However, we propose a tentative mechanism of the formation of 9,9′-methylenedithioxanthene in Scheme 5.

The separation of the reaction mixture by means of chromatographic technique was rather troublesome, especially in the later part of the column chromatography using polar solvents such as ether, ethyl acetate, acetone, and ethanol. Thianthrene or thioxanthene which was normally removed very rapidly when benzene was used as an eluant in the beginning. However, although large amount of benzene was used and the last benzene fraction did not have either compound, acetone or ethanol fraction showed always a spot corresponding to thianthrene or thioxanthene on a tlc plate. This result suggests a possible formation of a complex between sulfur containing compounds and mercury compound. This is consistent with the result in which some difficulties are involved in the separation of thianthrene or phenoxathiin from the reaction mixture containing organomercurials.[11]

The observation of free mercury only in dibenzylmercury reaction supports the formation of benzylmercury perchlorate which then undergoes a facile demercuration to form free mercury and a stable benzylcarbonium ion. An analogous reaction mechanism was attributed to the demercuration of alkylmercury (II) acetate in the presence of perchloric acid.[12]

The failure of observing free mercury in the reactions with dimethyl- and diphenylmercury was attributed to rather unstable methyl and phenyl cation. In fact, Kochi[10] found that only single alkyl group was removed from alkylmercury compounds such as dimethyl-, diethyl-, and methyl(alkyl) mercury and RH^+ were stable to further cleavage in acetic acid or acetonitrile.

To our knowledge methylmercury and phenylmercury perchlorate have never been isolated. Generally alkyl- and arylmercury perchlorate have been identified by conversion them into a corresponding chloride. However, some progress for obtaining methylmercury and phenylmercury perchlorate has been made through a series of tedious work. A crystal which was hygroscopic has been obtained from the reaction with dimethylmercury. ^1H nmr and ir data are consistent with the expectation from methylmercury perchlorate. In the meantime, a pale red crystal obtained from the reaction with diphenylmercury showed ^1H nmr and ir spectrum in good agreement with phenylmercury perchlorate. Repeated recrystallization did not help getting pure crystal. Consequently, measurement of mercury content by atomic absorption spectroscopy was not close to the theoretical value.

Acknowledgement. The authors are grateful to the Korea Science and Engineering Foundation for support of this work.

References

(1) H. J. Shine and L. Hughes, *J. Org. Chem.*, **31**, 3142 (1966).

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

(3) C. C. Price, M. Siskin and C. K. Miro, *J. Org. Chem.*, **36**, 794 (1971).

(4) M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.*, **21**, 1692(1973) and references are therein.

(5) K. Kim, *J. Korean Chem. Soc.*, **24**(1), 34 (1980).

(6) W. Rundell and K. Scheffer, *Tetrahedron Lett.*, 993 (1963).

(7) D. S. Matteson, "Organometallic Reaction Mechanisms of the Nontransition Elements", Academic Press, New York, N.Y., 1974.

(8) F. R. Jensen and B. Rickborn, "Electrophilic substitution in Organomercurials", McGraw-Hill, New York, N.Y., 1968.

(9) M. H. Abraham "Comprehensive Chemical Kinetics", Vol. 12, C. H. Bamford and C. F. H. Tipper, Ed., Chapter 7 and 8, 1973.

(10) J. Y. Chen, H. C. Gardner and J. K. Kochi, *J. Amer. Chem. Soc.* **98**, 6150 (1976).

(11) Private communication from Professor H. J. Shine.

(12) J. K. Kochi, Vol. 1, J. K. Kochi, Ed., "Free Radicals", Chapter 11, p. 611, Wiley-Interscience, 1973.