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Machanism on the Formation of Bis-9,9'-thioxanthylmethane from the Reaction of Thioxanthylum Ion with Dimethylmercury(I)

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9-Methylenethioxanthene(6) was synthesized and for the first time good mp and spectral data were taken. Reaction of (6) with thioxanthylum ion (1) in acetonitrile led to a carbenium addition adduct (8) which then was either attacked by a variety of nucleophiles subsequently added or underwent deprotonation reaction to give an olefin (13). From these reactions, was obtained bis-9,9'-thioxanthylmethane (2). These results indicate clearly that (2) can be formed via (8) by accepting hydride. Isolation of (2) and (6) from the reaction of (1) with 9-methylthioxanthylum ion (18) also supports the involvement of (8) in the reaction of (1) with dimethylmercury. However, addition of thioxanthene radical (4) to (6) has not been ruled out.

Introduction

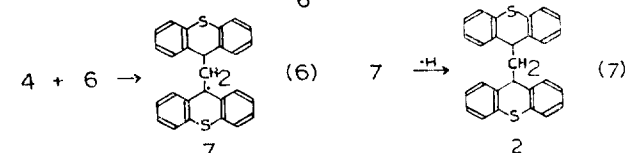
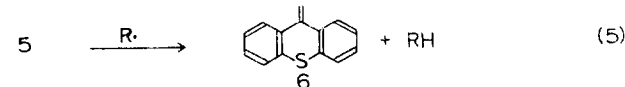
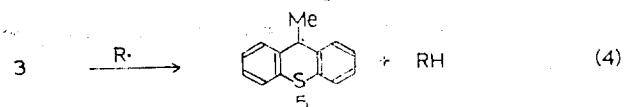
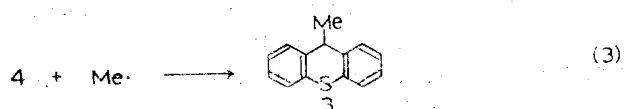
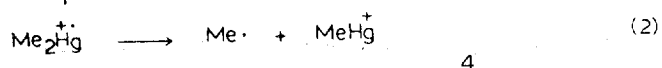
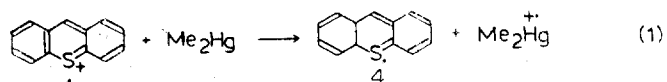
Thioxanthylum ion (1) prepared from the oxidation of thioxanthene by thianthrene cation radical perchlorate has been used to synthesize 9-arylthioxanthene and 9-thioxanthyl-phosphonium salts.¹ The products are believed to be formed by the nucleophilic attack of aromatics bearing an elect-

ron donating group and phosphines, respectively.

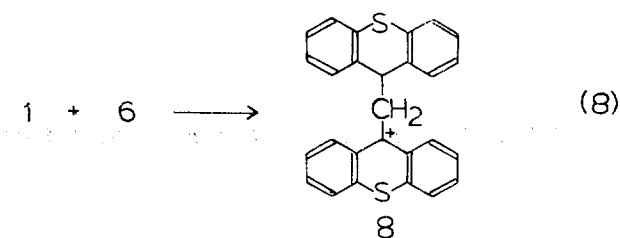
In contrast, the reactions of (1) with organomercurials were explained by an electron-transfer from organomercurials to (1), followed by a radical combination reaction between thioxanthene radical (4) and alkyl or aryl radical originated from organomercurials.² Therefore, from the reaction with diphenyl- and dibenzylmercury under N₂ atmosphere were

obtained 9-phenyl- and 9-benzylthioxanthene in good yields, respectively.

However, reaction with dimethylmercury afforded *bis*-9,9'-thioxanthenylmethane (**2**) instead of 9-methylthioxanthene (**3**). The mechanism for the formation of (**2**) was previously proposed without any concrete evidence as shown below:



The involvement of an electron transfer step, followed by radical combination to give (**3**) (eqs 1, 3) and decomposition of dimethylmercury cation radical (eq 2) were based on the experimental results obtained from author's laboratory, along with the other results reported.^{3,4} Analysis on the structure of (**2**) suggests that 9-methylenethioxanthene (**6**) must be formed as an intermediate, which then undergoes either a radical addition reaction to afford (**7**) or a carbenium addition to afford (**8**) (eq 8).



As the first step, a study on the carbenium addition reaction represented by eq 8 was undertaken. We wish to report in this paper the synthetic method of (**6**) and the reactions of (**6**) with (**1**).

Experimental

Thioxanthene (Pfaltz and Bauer) was used without further purification. Thioxanthone was obtained from Aldrich and purified on the silica gel (Merck, Kiesel gel 60, 70-230 ASTM mesh, 0.0200-0.063 mm Cat. No. 7734) using diethyl ether as an eluant. The compound was dried on P_2O_5 in vacuo. Thianthrene was obtained from Merck and its cation radical perchlorate was prepared according to Rundel and Schffer's method.⁵ 9-Benzylthioxanthene was prepared² from the reaction of (**1**) with dibenzylmercury which was obtained

from Alfa Products.

Methyl iodide was obtained from Kanto Chemical Corporation.

Perchloric acid (70 %) was Wako Pure Chemical Industry Ltd. extra pure.

Acetonitrile was Kanto Chemical Corporation extra pure and was refluxed with P_2O_5 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.

Tetrahydrofuran (THF) was obtained from Merck and predried on KOH pellet, followed by distillation. The distillate was refluxed with lithium aluminum hydride for 3 h. Dried THF was stored over sodium wire in a septum-capped bottle. Triphenylphosphine was Matheson & Collman reagent grade (mp 80-81°C).

Ultraviolet spectra were obtained using a Beckman Model 5720 UV-Vis spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Model 283 Infrared spectrophotometer. All infrared spectra were taken using potassium bromide pellets. ^1H nmr spectra were taken on Varian EM 360A spectrometer and are reported in parts per million (δ) downfield from tetramethylsilane. Melting points were measured on a Fisher-Jones melting point apparatus and are uncorrected.

Methyltriphenylphosphonium iodide (**9**). To a stirred solution of 11 g (42 mmol) of triphenylphosphine in 45 ml of benzene was added 8.23 g (56 mmol) of methyl iodide. The phosphonium salt formed in one day was filtered, followed by recrystallization from ethanol: mp 183-184.5°C (*lit.*⁶ 182°C).

Preparation of 9-methylenethioxanthene (**6**). To a solution of dried (**9**) (2.95 g, 7.3 mmol) in 30 ml of THF was added dropwise a solution of *n*-BuLi in THF (6.7 ml/10ml THF) during 5 min. under N_2 atmosphere. The mixture was heated at 66° for 30 min, followed by the addition of 2.17 g (10.2 mmol) of thioxanthone. This reaction mixture was refluxed for 1 hr and then cooled at room temperature. *n*-Hexane (100 ml) was added to the reaction mixture, which then was washed with water several times (Removal of oxygen from water by bubbling N_2 is critical for increasing yield of the product) until aqueous solution was neutral. The hexane layer was evaporated to dryness and the residue was chromatographed on silica gel (2×20 cm). Elution with *n*-hexane (100 ml) gave 1.1 g (5.3 mmol, 73 %) of (**6**): mp 47.5-48.5°C (pet. ether) (*lit.*⁷ sticky); IR/(KBr) 3050, 1605, 1433, 880, 755, 725 cm^{-1} ; ^1H NMR(CDCl_3) δ 5.56 (*s*, 2H, vinyl), 7.00-7.70 (*m*, 8H, aromatic); UV, λ_{max} 229, 266.5, 333 nm. This compound was unstable in the air.

Reaction of (**6**) *with* (**1**). To a stirred solution of thianthrene cation radical perchlorate (1.330 g, 4.21 mmol) in 30 ml of acetonitrile was added 0.416 g (2.10 mmol) of thioxanthene. Color turned immediately dark red and much solids were formed. To this mixture was added 0.440 g (2.10 mmol) of (**6**) and stirring was continued for 20 hr at room temperature. Color of the reaction mixture remained almost unchanged. Thin layer chromatography using benzene as eluant showed

three spots corresponding thianthrene, thioxanthone, and an unknown at the origin. Evaporation of the solvent using a rotary evaporator gave dark violet residue, which was chromatographed on silica gel column (2×20 cm). Elution with hexane (150 ml) gave 0.941 g (4.35 mmol) of thianthrene. Elution with ethyl ether (80 ml) gave 0.130 g (0.612 mmol) of thioxanthone. Upon addition of ethanol into the column, the dark violet color remained on the top of the adsorbent disappeared. However, the same color reappeared from ethanol fractions by evaporation completely. By adding ethanol again color disappeared and white solids were precipitated. The solids were recrystallized from ethanol, followed by a mixture of hexane and methylene chloride: mp 172.5–175.5°C; IR(KBr) 1460, 1065, 750 cm⁻¹; ¹H NMR (CDCl₃) δ 1.04 (t, 3H, methyl), 2.52 (d, 2H, methylene), 3.03 (q, 2H, o-methylene), 3.92 (t, 1H, methine), 6.40–7.80 (m, 16H, aromatic). This compound turns out to be 9-ethoxy-bis-9, 9'-thioxanthylmethane (10).

To the dark violet residue (8) obtained from ethanol fraction was added acetone. Dark violet color faded slowly. Evaporation of acetone in two days gave a white residue, which was recrystallized from ethanol, followed by a mixture of hexane and methylene chloride: mp 180.5–181.5°C; IR (KBr) 3050, 1720 (C=O), 1550, 760, 730 cm⁻¹; ¹H NMR (CDCl₃) δ 1.73 (s, 3H, methyl), 2.58 (d, 2H, methylene adjacent to methine H), 3.07 (s, 2H, methylene adjacent to C=O), 3.87 (t, 1H, methine), 6.50–7.45 (m, 16H, aromatic). This compound was assigned to be 9-acetyl-9,9'-bis-thioxanthylmethane (11).

Reaction of (8) with Absolute Ethanol. To a stirred solution of thianthrene cation radical perchlorate (0.733 g, 2.32 mmol) in 30 ml of acetonitrile was added 0.199 g (1.00 mmol) of thioxanthene, followed by 0.218 g (1.04 mmol) of (6). After the reaction mixture was stirred for 30 min. 2 ml of absolute ethanol was added and stirring was continued for 4 days at room temperature. Chloroform (70 ml) was added to the reaction mixture, which then was washed with water several times to remove perchloric acid. Evaporation of chloroform layer gave a residue which was chromatographed on a silica gel column (2×20 cm). Elution with *n*-hexane gave thianthrene, thioxanthene, (6), and 4 other products. Analysis of the mixture containing thianthrene and thioxanthene by ¹H NMR technique revealed that the mixture consisted of 0.473 g (2.19 mmol) of the former and 0.021 g (0.11 mmol) of the latter. The second hexane fraction gave only single compound, identified as 9-thioxanthyl-9'-methylene thioxanthene (12): mp 222–223.5°C (hexane+methylene chloride); IR (KBr) 3055, 1582, 1460, 1438, 1382, 762, 746, 732 cm⁻¹; ¹H NMR (CDCl₃) δ 4.90 (d, 1H, methine, J=11 Hz), 6.51 (d, 1H, vinyl, J=11 Hz), 7.10–7.87 (m, 16H, aromatic). The third hexane fraction gave a mixture of (12), (2), and an unknown, which could be separated nicely by fractional recrystallization from a mixture of hexane and methylene chloride. The melting point of (2) was 184–185°C and its ¹H NMR (CDCl₃) data was identical with those reported previously. The unknown compound showed a multiplet at δ 6.73–7.90 and mp was 188–189°C. Elution with benzene

gave 0.029 g (0.12 mmol) of thianthrene 5-oxide and 0.049 g (0.23 mmol) of thioxanthone.

Reaction of (8) with Acetone. To a stirred solution of (1) prepared from the reaction of 0.733 g (2.32 mmol) of thianthrene cation radical perchlorate with 0.199 g (1.00 mmol) of thioxanthene in 30 ml of acetonitrile was added 0.218 g (1.04 mmol) of (6). After stirring was continued for 4 days, 2 ml of acetone was added. Color turned slowly brown. The reaction mixture was worked up as usual in 8 days. Elution with hexane gave 0.480 g (2.22 mmol) of thianthrene and 0.002 g (0.01 mmol) of thioxanthene. Elution with benzene gave a mixture, consisting (11) and a sticky material of which separation using basic alumina has been unsuccessful. Elution with ethanol gave 0.176 g of solid, which was recrystallized successively from methylene chloride-hexane, and methylene chloride-methanol: mp 252.5–254.5°C (sublimation starts at 238°C); ¹H NMR (CDCl₃) δ 1.79 (s, 6H, 2 methyl) 1.93 (s, 4H, 2 methylene of acetyl group), 3.14 (s, 4H, methylene of propanone), 6.76–7.35 (m, 16H, aromatic). IR(KBr) 3060, 3000, 2940, 1725, 1706, 1587, 1476, 1420, 1360, 1270, 1160(br), 1100(br), 760, 740, 726, 690, 612 cm⁻¹. This compound was identified to be 1,3-(bis-9-acetylthioxanthyl)-2-propanone (13).

Reaction of (81) with Water. To a stirred solution of (1) prepared from the reaction of 0.469 g (1.49 mmol) of thianthrene cation radical perchlorate with 0.332 g (1.67 mmol) of thioxanthene in 30 ml acetonitrile was added 0.158 g (0.713 mmol) of (6), followed by 2 ml of water. This mixture was stirred for 10 days at room temperature and color turned purple. The reaction mixture was worked up as before and the residue was chromatographed on a silica gel (2×20 cm) column. Elution with hexane (140 ml) gave 0.271 g (1.25 mmol) of thianthrene, 0.025 g (0.13 mmol) of thioxanthene, 0.033 g (0.15 mmol) of thioxanthone, and 0.011 g (0.27 mmol) of (2). Elution with benzene (80 ml) gave 0.229 g of a unknown compound. Recrystallization from methylene chloride, hexane, pet. ether, methanol, or ethanol was unsuccessful. However, the solid obtained from the mixture of methanol and methylene chloride melted at 187–191°C. Repeated recrystallization using the same solvent raised melting point to 211.5–219.5°C. This compound was assigned to be 9-methoxy-bis-9, 9'-thioxanthylmethane (14) in view of the following spectral data: IR(KBr) 3060, 2980, 2900, 1580, 1440, 1385, 1120, 1070, 750 cm⁻¹; ¹H NMR (CDCl₃) δ 2.50 (d, 2H, methylene), 2.90 (s, 3H, methyl), 3.84 (t, 1H, methine), 6.40–7.73 (m, 16H, aromatic.)

Reaction of (8) with 9-benzylthioxanthene. To a stirred solution of (1) prepared from the reaction of 1.464 g (4.64 mmol) of thianthrene cation radical perchlorate with 1.044 g (5.26 mmol) of thioxanthene in 30 ml of acetonitrile was added 0.447 g (2.12 mmol) of (6). After four days stirring, 0.400 g (1.39 mmol) of 9-benzylthioxanthene was added. The mixture was continually stirred for 2 months and worked up as before. Elution with hexane (200 ml) gave 1.016 g (4.70 mmol) of thianthrene, 0.499 g (2.51 mmol) of thioxanthene, 0.098 g (0.46 mmol) of thioxanthone, 0.363 g (1.20 mmol) of 9-benzylthioxanthene, 0.156 g (0.38 mmol) of (2). Elution with

toluene and ethyl ether gave 0.052 g and 0.048 g of sticky materials, respectively, which have been unidentified. Elution of ethyl acetate gave 0.271 g of a mixture, from which 0.141 g of inorganic perchlorate was isolated. Acetone fraction was divided and treated in different ways: (a) Addition of methanol to 0.444 g of the sticky violet residue caused color change to colorless. After water was added to the colorless methanol solution, it was extracted with benzene. The benzene soluble material was chromatographed on silica gel. From hexane and benzene fractions were obtained 0.037 g of (6) and 0.110 g of (11), respectively. (b) The sticky violet material was recrystallized from acetic acid. Dark violet solid with green fluorescence was obtained. Proper NMR solvent has not been found. (c) Treatment of the sticky violet material (0.228 g) with ethanol gave colorless residue which was chromatographed as usual.

Elution with hexane gave 0.015 g of a mixture of thioxanthone and (6). ^1H NMR spectrum of the latter hexane fraction (0.036 g) showed a singlet at δ 5.37 and a multiplet in the aromatic region. This indicated the formation of benzyli-dene-thioxanthene (15).⁸

Elution with benzene gave 0.111 g of a sticky material, from which (11) was obtained. (d) Treatment of the dark violet residue with acetone resulted in colorless solution in 2 days. This mixture was worked up as usual.

Elution with hexane gave 0.014 g (0.07 mmol) of (6) and small amount of (15) was also obtained. From benzene fraction was obtained also (11).

*Preparation of (1).*⁹ To a suspension of 5 g (24 mmol) of thioxanthone in 75 ml of boiling methanol was added slowly sodium borohydride. As the reaction proceeds undissolved thioxanthone disappears and yellow color becomes faded. After yellow color disappeared completely water was added and then the aq. solution was extracted with benzene.

Evaporation of benzene gave thioxanthene-9-ol (16), which was dissolved in CH_2Cl_2 , followed by the addition of hexane. As CH_2Cl_2 evaporates slowly, good crystal of (16) was obtained. Compound (16) (1.6 g, 7.5 mmol) was dissolved in 25 ml of ethyl ether and then cooled to -70°C . Addition of 5 ml of 70% perchloric acid to the cooled solution of (16) gave orangish red crystal (1), which was filtered and worked up with acetic acid, followed by ethyl ether. Recrystallization of (1) from acetic acid caused color change and poor recovery.

*Preparation of 9-Methylthioxanthylum Perchlorate (17).*⁹ Grignard reagent, prepared from a reaction of 1.9 ml (30 mmol) of methyl iodide and 1 g of magnesium in 75 ml ethyl ether was added 3 g (14 mmol) of thioxanthone in 50 ml benzene. This mixture was refluxed for 5 h, followed by washing with water. Evaporation of ether afforded a sticky oil which was immediately dissolved in 50 ml of ethyl ether, followed by cooling to -70°C . Addition of 5 ml of 70% perchloric acid gave red crystal which was filtered and washed with acetic acid. Recrystallization from acetic acid gave red crystal (17).

Reaction of (1) with (17). To a stirred solution of 0.678 g (2.28 mmol) of (1) in 30 ml of acetonitrile was added 0.711 g (2.28 mmol) of (17). This mixture was continually stirred for

77 hr and then addition of water caused color change to violet. This aq. solution was extracted with chloroform. The residue from chloroform was chromatographed on silica gel (1.9 \times 20 cm). Elution with hexane gave 0.007 g (0.04 mmol) of thioxanthene, 0.039 g (0.19 mmol) of (6), 0.043 g (0.11 mmol) of (12), 0.039 g (0.10 mmol) of (2).

Elution next with benzene gave 0.036 g (0.14 mmol) of thioxanthone and 1.028 g of a mixture, mainly consisting of 9-hydroxy-bis-9,9'-thioxanthenylmethane (18), which was recrystallized from a mixture of methylene chloride and hexane: mp $180\text{--}183^\circ\text{C}$; ^1H NMR(CDCl_3) δ 2.28 (*d*, 2H, methylene), 2.30 (*s*, 1H, hydroxy), 3.89 (*t*, 1H, methine), 6.52–7.93 (*m*, 8H, aromatic).

Results

(A) Preparation of 9-methylenethioxanthene (6).

The compound (6) was synthesized rather in good yield (73%) and characterized for the first time with spectral data and melting point. However, it was unstable in the air and unable to be kept for a long time without decomposition.

(B) Reaction of (6) with thioxanthylum ion (1).

Addition of (6) to (1), generated from an electron transfer between thianthrene cation radical and thioxanthene afforded 9-(9'-thioxanthenylmethyl) thioxanthylum ion (8), which was stable enough to be separated by column chromatography to give a dark violet residue from ethanol fraction. So, treatment of the dark violet residue with ethanol and acetone led to 9-ethoxy-bis-9,9'-thioxanthenylmethane (10) and 9-acetonyl-bis-9,9'-thioxanthenylmethane (11), respectively. From addition of absolute ethanol directly to the reaction mixture in solution state before evaporation of the solvent for chromatography were isolated two interesting compounds, (2) and (3) among others but unexpectedly compound (10) was not isolated.

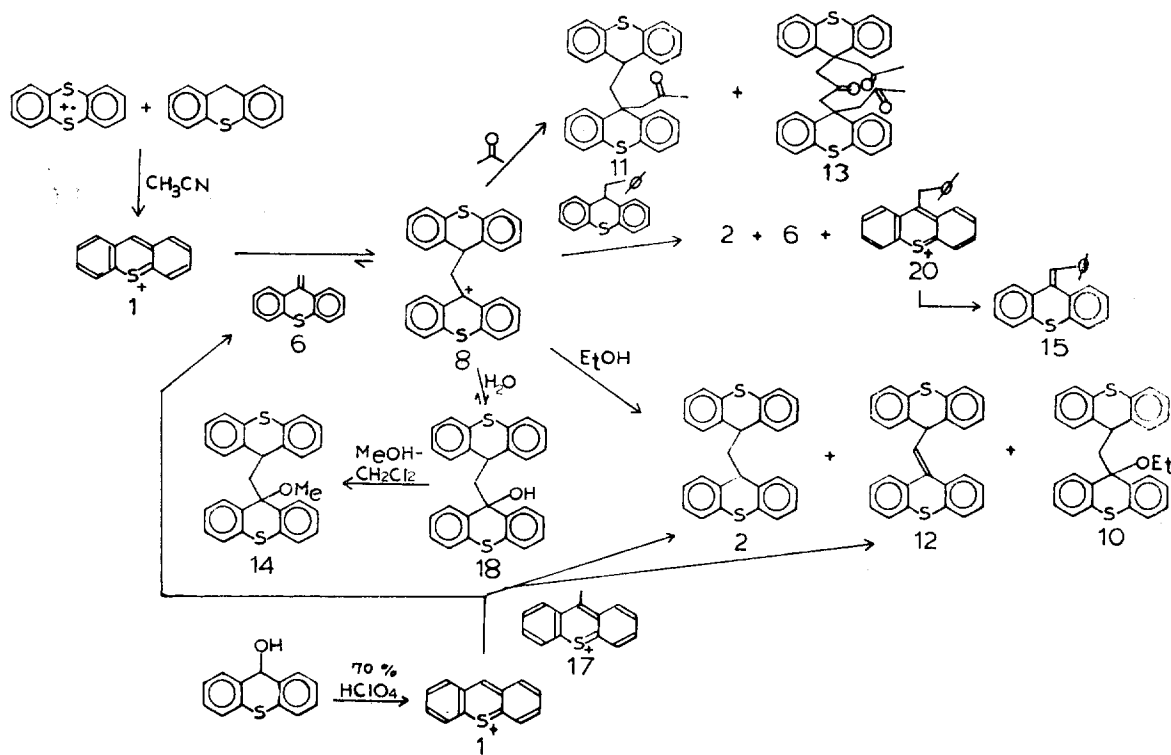
In order to understand more thoroughly the chemical behavior of (8), reactions with water and acetone were carried out. In addition, a reaction with 9-benzylthioxanthene was undertaken simply because it was believed to be a better hydride donor than thioxanthene. 9-Methylthioxanthylum ion (17) was added to the solution of (1) in CH_3CN to demonstrate the generation of (6) and other related products obtained from *in situ* reaction.

The results are summarized in the following Scheme 1.

Discussion

As mentioned earlier (eq. 1–7), the formation of (2) makes inevitably an assumption that (6) has to be formed as an intermediate by either electrophilic or free radical addition to olefin which are one of the thoroughly studied field in organic chemistry. Therefore, addition of either (4) or (1) to (6) is reasonably expected to give the corresponding a radical adduct (7) or carbenium adduct (8).

The evidences in which the formation of (3) is followed by a radical combination came mainly from the drastic change on the yield of thioxanthone in the reaction with dibenzylmercury depending on the oxygen content in the reaction medium together with other factors.²

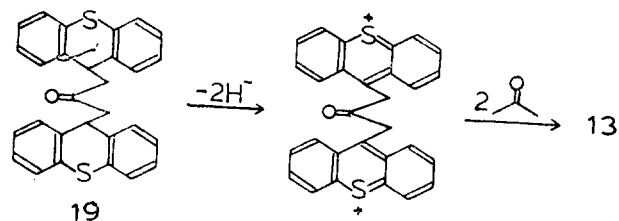
Scheme 1. Summary in the reaction of (1) with (6), followed by some nucleophiles and with (17).

Radical combination mechanism was also proposed in the reaction of 9-phenylthioxanthylum ion with Grignard reagents.¹⁰ In order to uncover the ambiguity on the species participating in the addition reaction, (1) was generated using thianthrene cation radical perchlorate and thioxanthenone as reported previously,¹ and then let it react with (6) which was synthesized via an independent route.

The isolation of (10) and (11)¹¹ indicates that the dark violet residue obtained from ethanol fraction must contain a carbenium adduct (8). The carbenium ion (8) is fairly stable in the acidic solution and also it can remain unchanged even on a silica gel column. It seems likely that a portion of (8) reacts with ethanol during the process of chromatography in view of a color change from dark violet to colorless. For the purpose to prevent the reaction from occurring on silica gel the reaction mixture containing (8) was quenched by adding absolute ethanol and acetone, respectively. As shown in Scheme 1, no ethanol substituted product (10) was obtained. Instead, (12), a deprotonated product and (2) were obtained. The formation of (12) is indeed another evidence for the intermediacy of (8) where ethanol acts as a base. Compound (2) can be formed from a hydride transfer to (8). Similar reaction has been reported: reaction of 9-alkylxanthylum with ethanol at room temperature gave 9-alkyl-9-ethoxyxanthene. However, at reflux temperature was obtained 9-alkylxanthene.¹²

The source of hydride in this reaction is believed to be thioxanthenone. Nevertheless, the hydride transfer process may be a highly energetic process because the reactions with acetone do not give (2). Instead, compound (11) and a new compound (13) were formed. Therefore, enolized acetone

may be a better nucleophile than ethanol for the carbenium ion (8). This result suggests that (2) may not be formed in the presence of good enolizable nucleophiles. The formation of (13) can be explained by hydride transfer from *bis*-1,3-(9-thioxanthenyl)-2-propanone (19), followed by nucleophilic attack by enolized acetone.



Compound (19) was synthesized from the reaction of (1) with acetone in the author's laboratory.¹³ Compound (2) was also obtained from the reaction with water, but surprisingly, compound (14) was isolated from a mixture of methanol and methylene chloride as a final solvent after a series of attempted recrystallizations of the benzene fraction. Consequently, compound (14) is believed to be formed by an exchange reaction between hydroxy group of 9-hydroxy-bis-9,9'-thioxanthenylmethane (18) and methanol.

One can expect that the amount of (2) is increased in the presence of a good hydride donor. In order to ascertain this expectation, 9-benzylthioxanthenone which is not only an analogous compound to thioxanthenone but also has a methine hydrogen at 9-position was added to the reaction mixture as usual. But our results were not in good agreement with that anticipated although yield of (2) was increased somewhat. This reaction gave a violet residue which was believed to be consisting of (8) and 9-benzylthioxanthylum ion (20) even

after elution with acetone. These reaction intermediates, (8) and (20) were trapped using nucleophiles, *e.g.* methanol, acetone, and ethanol. Isolation of (6) in three nucleophilic reactions indicates that addition reaction of (1) to (6) is reversible. Furthermore, formation of (15) implies that a hydride transfer from 9-benzylthioxanthene is followed by ready deprotonation to give (15).

In order to see if (2) could be formed from (17), (1) and (17) were synthesized according to the modified Price's method.⁹ Reaction between two different ions gave compound (2) in addition to compounds, (6), (12), and (18), *etc.*¹⁴

In conclusion, the formation of (2) in the reaction of (1) with dimethylmercury can be explained by the addition reaction of (1) to (6) which is formed by deprotonation of (17). The compound (17) is believed to be formed from a hydride transfer of 9-methylthioxanthene, which is a radical combination product of thioxanthene and methyl radicals.

However, at this moment, we can not rule out the possible involvement of a radical addition reaction (aq. 6, 7).

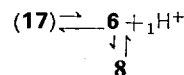
A study on this unsettled question is in progress.

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 (14) One of referees suggested that perhaps (17) could be in an equilibrium with (6), which would then undergo the same type of reaction with 1 as shown below:



The Kinetics and Mechanism of Nucleophilic Addition of Thioglycolic Acid to β -Nitrostyrene Derivatives

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The rate constants of the nucleophilic addition of thioglycolic acid to the derivatives (H, p-CH₃, p-CH₃O, p-Cl, p-NO₂) of β -nitrostyrene were determined by ultraviolet spectrophotometry. The rate equations which can be applied over a wide pH range were obtained. Therefrom a reaction mechanism was proposed. Above pH 8.5, sulfide anion adds to the double bond (Michael type addition). However, below pH 8.5, the neutral molecule and HSCH₂COO[⊖] add to the double bond.

Introduction

When the electron density of a carbon-carbon double bond is reduced by electron-withdrawing substituents, nucleophilic attack at one of the vinylic carbons may occur. In general, the mechanisms of nucleophilic additions to double bonds have not been as much studied or systematized as those of electrophilic addition.¹⁻⁷

In order to verify the mechanism of this type of reaction, we have investigated the addition of *n*-propylmercaptan and hydrogen cyanide to α -cyano- β -piperonylacrylic acid.⁸⁻⁹

The present investigation is a study of kinetics of the addition of thioglycolic acid to β -nitrostyrene derivatives. An attempt has been made to interpret findings in these reactions.

Experimental

β -Nitrostyrene derivatives were prepared by condensation of corresponding benzaldehyde derivatives and nitromethane.¹⁰ Thioglycolic acid (E. Merck) was used without further purification. All buffer solutions were prepared from reagent

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