삼아릴-9-티오클리태닐포스포니움 과염소산염의 아릴기에 의한 상자기성 벗김 효과

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**Paramagnetic Deshielding Effects by Aryl Groups of Triaryl-9-thioxanthenylphosphonium Perchlorate**

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요약. 삼페닐-9-티오클리태닐포스포니움 과염소산염과 삼오르토-메톡시태닐-9-티오클리태닐포스포니움 과염소산염과 대조적으로 삼아릴-9-티오클리태닐포스포니움 과염소산염은 각각 55.58 ppm과 55.70 ppm 에서 methine 양성자에 해당하는 이중상을 보여주었다. 이 값은 9-아릴티오클리태닐의 상응값 (55.05 ~ 5.30) 보다 다소 큰 값이나 방향족합성물의 양성자의 값과는 분명히 차이가 난다.

이 결과는 삼아릴-9-티오클리태닐포스포니움 과염소산염의 methine 양성자가 낮은 장으로 이동한 원인이 전자가 부족한 인산자에 의한 유반 효과 때문이 아니라 인산자 결합된 세개의 아릴기의 상자기성 벗김 효과에 의한 것임을 의미한다.

**ABSTRACT.** In contrast with pmr (only multiplets at 56.6~7.8 ppm) spectrum of triphenyl-9-thioxanthenylphosphonium perchlorate and tri-o-methoxyphenyl-9-thioxanthenylphosphonium perchlorate, tri-n-butyl-9-thioxanthenylphosphonium perchlorate and tribenzyl-9-thioxanthenylphosphonium perchlorate showed a doublet at 55.58 and 55.70 ppm, respectively, assigned to a methine proton. This value is slightly larger than the corresponding values (55.05 ~ 5.30) of 9-aryltioxanthenes but clearly differentiated from those of aromatic protons.

This result implics that the downfield shift of a methine proton of triaryl-9-thioxanthenylphosphonium perchlorate is not due to inductive effects of an electron deficient phosphorus atom but paramagnetic deshielding effects by three aryl groups on phosphorus.

**INTRODUCTION**

Of the synthetic methods of phosphonium salts, reactions of carbonium salts with tertiary phosphines have long been known as shown below:

\[
\text{R}^+\text{C}^+\text{X}^- + \text{Ph}_3\text{P} \rightarrow (\text{Me}_2\text{NPh})_2\text{C}^+\text{X}^- + \text{Ph}_3\text{P}
\]

However, some carbonium ion such as trietho-
Thei$^-9$-thioxanthenylphosphonium perchlorate has been known as an alkylating reagent only.\textsuperscript{2}

$(\text{EtO})_2\text{C}^+\text{BF}_4^- + \text{R}_3\text{P} \rightarrow \text{R}_3\text{P}^+\text{EtBF}_4^- + (\text{EtO})_2\text{O}$

We have shown that thioxanthylum cation, generated in situ by mixing thianthrene cation radical perchlorate with thioxanthene in acetonitrile, reacted with triphenylphosphine to give triphenyl-9-thioxanthenylphosphonium perchlorate.\textsuperscript{3} Pmr spectrum of the perchlorate salt taken in DMSO-$d_6$ solution showed only multiplets in the region of $\delta 6.6$~$7.8$ ppm. The expected methine proton signal was not observed near $\delta 5$ ppm in which 9-arylsubstituted thioxanthenes such as 9-(p-methoxyphenyl)thioxanthene, 9-(p-N,N-diethylaminomethyl)thioxanthene, and 9-phenylthioxanthene showed a singlet of a methine proton. The structure of this phosphonium salt was confirmed simply by the reaction with alcoholic potassium hydride, which gave quantitatively triphenylphosphine oxide and thioxanthene as decomposed products. The isolation of these decomposed products indicated that the perchlorate salt consisted of thioxanthene and triphenylphosphine moiety even though pmr spectrum exhibited only multiplets between $\delta 6.6$ and $7.8$ ppm. We gave a reason for the disappearance of a methine proton signal as an inductive effect by an electron deficient phosphorus atom which is in position to the methine proton.

There are much pmr and $^{31}$P nmr data on phosphonium salts.\textsuperscript{2} Most of pmr data in the literature concern mainly methyl, ethyl, and vinyl protons of the phosphonium salts. However, little has been studied on methine proton. Therefore, we felt that further pmr study on phosphonium salt bearing a methine proton was necessary. This paper describes the reason for downfield shift of a methine proton of triphenyl-9-thioxanthenylphosphonium perchlorate and its analogues and some other results.

**EXPERIMENTAL.**

**Materials.**

Thioxanthene was obtained from Pfaltz and Bauer Co. and used without further purification. Thianthrene was synthesized from benzeno, sulfur, and anhydrous aluminum chloride by Jeong's modified method.\textsuperscript{4} Thianthrene cation radical perchlorate was prepared by the method of Rundel and Scheffer.\textsuperscript{5} Triphenylphosphine was from Matheson Coleman and Bell (m.p, 80~81°C). Tri-$n$-butylphosphine was Kanto Chemical Co. GR grade. Chlorodiphenylphosphine was obtained from Merck (Art. 810155). Tri-$o$-methoxyphenylphosphine was prepared by the reported method and had m.p 203~204 °C (lit.\textsuperscript{6} 203~204 °C). Tribenzylphosphine was prepared by Hinton's method\textsuperscript{7} but the compound was very sensitive to the air, forming the corresponding oxide. Accordingly, the crude product obtained under nitrogen atmosphere was used without further purification. Acetonitrile was Kanto Chemical Co. Extra pure and was refluxed with phosphorus pentoxide for 2 hr, followed by distilling twice. Dried acetonitrile was stored over molecular sieve(4 Å) in a septum-capped bottle. $n$-Hexane, benzene, diethyl ether, acetone, and methanol were obtained from Kanto Chemical Co. and Wako Pure Chemical Industry Ltd. These solvents were redistilled before use. Deuterated nmr solvents were obtained from Aldrich Chemical Co.

**Apparatus.**

Thin layer chromatography (tlc) was performed on a glass plate ($2 \times 8$cm) with Merck Kiesel 60 PF$_{254}$ Silansiert (Art 7751). The slurry of the adsorbent was made in a mixture of chloroform and methanol (2:1, v/v). The chromatogram was visualized by mineral UV lamp.
Column chromatography was performed with Merck Silica Gel, 70–235 ASTM mesh, 0.05~0.2 mm (Art. 7734). Eluant solvents are specified in each case.

Ultraviolet spectra were obtained using Hitachi 124 and Beckman Model 3270 spectrophotometers. Infrared spectra were obtained with Jasco Model IR-G, Perkin–Elmer Model 710B, and Perkin–Elmer Model 823 infrared spectrophotometers. All infrared spectra were taken using potassium bromide pellets.

Pmr spectra were recorded using Varian EM 360 A spectrometer. Pmr chemical shifts were measured in ppm relative to an internal standard TMS.

Melting points were recorded using Fisher–Jones melting point apparatus and were not corrected.

Elemental analysis relied on Department of Chemistry, University of New Mexico, Albuquerque, NM, USA.

Reactions.

1 Reaction of Thioxanthylum Perchlorate with Tri-α-butyl-phosphine. To the solution of 1500 mg (5.03 mmol) of thianthrene cation radical perchlorate in 30 ml of acetonitrile was added 530 mg (2.67 mmol) of thioxanthene. The color of the stirred solution turned dark red and subsequent addition of 1452 mg (7.17 mmol) of tri-α-butylphosphine caused the solution pale yellow. After the solvent was removed under vacuum, the residue was chromatographed on the silica gel column (1.8×20 cm). Elution with benzene (250 ml) gave 1110 mg of a mixture of thianthrene and thioxanthene. Elution with ether (100 ml) gave 150 mg of yellow sticky material, identified as thianthrene 5-oxide. Acetone fraction (100 ml) gave a mixture of an unknown compound and yellow liquid, which was recrystallized from methanol to give 500 mg (1.18 mmol) of a crystalline solid, identified as tri-α-butyl-9-thioxanthenylphosphonium perchlorate, m.p. 150.5 ~ 151.5°C. Yield: 47%. UV λ_max 264 (br) nm. Pmr (CDCl_3) δ: 0.80 (t, 9H, methyl, J=6 Hz), 1.13 (m, 12H, methylene), 2.13 (m, 6H, methylene), 5.6 (d, 1H, methine, J'=17 Hz), and 7.12 ~ 7.84 (m, 8H, thioxanthene).

Analysis. Calculated for C_{25}H_{36}ClO_4 : C, 60.17 ; H, 7.27. Found : C, 60.85 ; H, 7.43.

2 Reaction of Thioxanthylum Perchlorate with Tri-o-Methoxyphenylphosphine. To the solution of 1785 mg (5.65 mmol) of thianthrene cation radical perchlorate in 30 ml of acetonitrile was added 571 mg (2.83 mmol) of thioxanthene. After the color of the cation radical had disappeared, 1609 mg (4.57 mmol) of tri-o-methoxyphenylphosphine was added. The dark red color disappeared in a minute. The solvent was evaporated to dryness under vacuum and then the residue was chromatographed on the column (1.8×20 cm). Elution with hexane (300 ml) gave 1138 mg (5.26 mmol) of thianthrene. Subsequent elution by ether (100 ml) gave 135 mg (0.64 mmol) of thianthrene 5-oxide. Elution with acetone (100 ml) gave 2825 mg of a sticky material which showed three spots with Rf value (CHCl_3): 0.0, 0.25, and 0.5, respectively. Addition of small amount of ethylene chloride to the material, followed by the filtration of ethylene chloride insoluble solid afforded 53 mg of a white solid which showed two characteristic bands of perchlorate at 1080 ~ 1140 and 620 cm^-1. This solid turned out to be an inorganic perchlorate in view of very simple infrared spectrum. We do not know the source of cation.

Methylene chloride in the filtrate was evaporated to dryness, followed by washing the residue with benzene afforded 429 mg (1.22 mmol) of tri-o-methoxyphenylphosphine. The benzene insoluble material was recrystallized from methanol.
thanol to give 100 mg (1.62 mmol) of a white solid, identified as tri-o-methoxyphenyl-9-thioxanthenylphosphonium perchlorate. m.p. 207.5~209.2°C (dec). Yield : 56%.

\[ \text{Pmr (CDCl}_3\text{)} \delta : 3.48(s, 9H, methoxy) \text{ and } 6.60~7.39(m, 21H, aromatic and methine) \text{ ppm. UV } \lambda_{max} 264 \text{ and } 291 \text{ nm.} \]

**Analysis.** Calculated for C_{24}H_{32}ClO_{4}PS : C, 62.91; H, 4.65. Found, C, 62.70; H, 4.62.

(3) **Reaction of Thioxanthylum Perchlorate with Tribenzylphosphine.** To the solution of 507 mg (1.61 mmol) of thianthrene cation radical perchlorate in 25 ml was added 199 mg (1.00 mmol) of thioxanthene. The solution of the reaction mixture was yellowish brown in a few minutes. Subsequent addition of about 1 g (ca. 3.29 mmol) of crude tribenzylphosphine to the reaction mixture caused the solution pale yellow, which showed four spots with Rf value (benzene) 0, 0.2, 0.4, and 0.7, respectively. After the solvent was evaporated to dryness, the residue was chromatographed on the silica-gel column (2×12 cm). Elution with hexane (300 ml) gave 419 mg of a mixture of thianthrene and thioxanthene. Elution next with benzene (130 ml), followed by ether (175 ml) gave small amount of an unidentified solid. Subsequent elution with ethanol (160 ml) gave 764 mg of a mixture of tribenzylphosphine oxide containing perchloric acid. Finally acetone fraction (330 ml) gave 462 mg (0.78 mmol) of a white solid, identified as tribenzyl-9-thioxanthenylphosphonium perchlorate. m.p (dec). 248.5~250.5°C (MeOH); Yield : 78%.

\[ \text{Pmr (DMSO-}d_6+\text{CDCl}_3) \delta : 3.61(d, 6H, benzyl, } J=13 \text{ Hz), 5.70(d, 1H, methine, } J=14 \text{ Hz), and 6.67~7.25(m, 23H, aromatic). UV } \lambda_{max} 260 \text{ and } 290 \text{ nm.} \]

**Analysis.** Calculated for C_{34}H_{30}ClO_{7}PS : C, 67.94; H, 5.03. Found, C, 67.85; H, 5.18.

(4) **Reaction of Thioxanthylum Perchlorate with Chlorodiphenylphosphine.** (a) To the solution of 1321 mg (4.18 mmol) of thianthrene cation radical perchlorate in 25 ml of acetonitrile was added 480 mg (2.42 mmol) of thioxanthene. The solution became dark red and 1.3 ml (ca. 7.03 mmol) of chlorodiphenylphosphine was added. The color of the solution became colorless, followed by yellowish brown. The solvent was evaporated to dryness, affording dark red residue. In order to transfer this residue completely into the column, the residue was dissolved in small amount of acetone and then the solution was adsorbed on silica gel. After the acetone was stripped off under vacuum the residue was able to be easily transferred into the column (2×12 cm). Elution with hexane (300 ml) afforded 975 mg of a mixture of thianthrene and thioxanthene. Elution with benzene (250 ml) gave 202 mg of a white solid, identified as 9-acetylthioxanthene, m.p 83.5~84.5°C (aq. MeOH); Yield : 38%.

\[ \text{Pmr (CDCl}_3\text{)} \delta : 1.90(s, 3H, methyl), 2.90 \text{ (d, 2H, methylene } J=8 \text{ Hz), 4.70(t, 1H, methine, } J=9 \text{ Hz), and 7.13~7.62(m, 8H, aromatic) ppm. IR (KBr) cm}^{-1} : 1710 \text{ (C=O). UV } \lambda_{max} 263 \text{ nm.} \]

**Analysis.** Calculated for C_{16}H_{18}OS : C, 75.85; H, 5.17; S, 12.66. Found, C, 75.56; H, 5.56; S, 12.60.

Elution with ether (100 ml) afforded 26 mg of diphenylphosphinic acid containing trace amount of thianthrene 5-oxide. Elution with ether (100 ml) afforded a sticky material, which was washed with methanol, followed by recrystallization from acetonitrile to give 200 mg of a white solid, identified as diphenyl-9-thioxanthenylphosphonium oxide. It did not melt at 300°C. Pmr (CDCl_3) \delta : 5.07(d, 1H, methine, J=24 Hz), and 7.00~7.67 (m, 18H, aromatic) ppm.

IR (KBr) cm\(^{-1}\) : 1180\(^{\circ}\)(P=O). UV \( \lambda_{max} \), 224
nm. Yield: 78 %.

Analysis. Calculated for C_{32}H_{36}OPS·C, 75.51; H, 4.78. Found. C, 75.47; H, 4.59.

Elution with methanol (100 ml) afforded 738 mg (3.38 mmol) of diphenylphosphinic acid, recrystallized from methanol giving m.p. 191 ~ 193 °C (lit. 9 194 ~ 196 °C).

UV λ_{max} 272, 265, and 224 nm. IR (KBr) O 6 cm⁻¹: 3000, 2150, 1670, and 960 (FOH).

(b) To the solution of 1276 mg (4.04 mmol) of thianthrene cation radical perchlorate in 25 ml of acetonitrile was added 420 mg (2.12 mmol) of thioxanthene. After the color of the solution became dark red, 1.2 ml (ca. 6.49 mmol) of chlorodiphenylphosphine was added. Dark red color turned yellow. Addition of 1.5 ml (13.7 mmol) of benzylamine caused the color of the solution to be colorless. The reaction mixture was worked up as in the previous reaction. Elution with hexane (300 ml) afforded 781 mg of a mixture of thianthrene and thioxanthene. Elution with benzene (250 ml) gave 77 mg of thianthrene containing small amount of thioxanthene and thianthrene 5-oxide. Elution next with ether (100 ml) gave 480 mg of a mixture of diphenylphosphinic acid and an unknown. This mixture was recrystallized from ethanol to give 36 mg of a crystalline solid whose m.p (dec) was 291 ~ 292.5 °C. UV λ_{max} 220 nm. Pmr (CDCl₃) δ: 7.6 ~ 6.2 (m) ppm. Further structural identification has not been made.

From acetone fraction (100 ml) was obtained a mixture of diphenylphosphinic acid and benzylamine hydroperchlorate, which was washed with acetonitrile to give benzylamine hydroperchlorate. The hydroperchlorate was recrystallized from a mixture of methylene chloride and hexane to afford 288 mg (1.24 mmol) of pure compound, confirmed by the comparison of the spectroscopic data with those of the authentic sample. The hydroperchlorate was also obtained from methanol fraction (1668 mg, 11.6 mmol). The white solid remained on the top of the adsorbent was taken out and dissolved in acetic acid. After acetic acid was removed under vacuum, 316 mg (0.79 mmol) of diphenyl-9-thioxanthenylphosphine oxide was obtained. Yield was 37 %.

RESULTS

We have run the reactions of thioxanthylum ion with several phosphines which was chosen for the purpose of the followings: (a) Good pmr signals other than aromatic protons should be observed from the phosphonium salt so that one could identify easily the formation of the expected product by pmr spectrum. Alkylyphosphine has a twofold advantage for this purpose: it could give signals of methyl and methylene protons. Alkyl groups are different from phenyl groups in terms of inductive and resonance effects. (b) It has been known that phenyl group can act as either an electron-donating or an electron-withdrawing group. Accordingly, in the case of triphenyl-9-thioxanthenylphosphonium perchlorate, it is hard to say whether three phenyl groups on phosphorus atom belong to the former or the latter. In order to enhance electron density at phosphorus atom and thus to bring about a decreasing inductive effect of an electron deficient phosphorus atom, tri-α-methoxyphenylphosphine was synthesized and the corresponding phosphonium salt was investigated. (c) Induced ring current by the π-electrons within the phenyl rings makes the resonance of the protons at downfield. This downfield shift occurs not only to the aromatic protons but also other protons which are not directly attached to the phenyl rings if those protons are under the influence of the induced magnetic field. Chlorodiphenylphosphine has two phenyl groups and thus induced magnetic
Table 1. Pmr chemical shifts of aryl-and alkyl-9-thioxanthenyl phosphonium salts and diphenyl-9-thioxanthenylphosphine oxide.

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>Phosphonium Perchlorate</th>
<th>Methine H, ppm</th>
<th>Other H, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Bu₃P</td>
<td>n-Bu₂P ClO₄</td>
<td>5.58</td>
<td>5.80 (4.5H, J=58Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d,1H, J=175Hz)</td>
<td>6.12 (5.1H, J=128Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.12 - 7.84 (m, 8Hz)</td>
<td></td>
</tr>
<tr>
<td>Ph₃P</td>
<td>Ph₂P ClO₄</td>
<td>3.48 (3.9H)</td>
<td>6.60 - 7.89 (m, 21H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d,1H, J=142Hz)</td>
<td>6.67 - 7.75 (m, 22H)</td>
</tr>
<tr>
<td>Ph₃P</td>
<td>Ph₂P ClO₄</td>
<td>3.70 (d,6H, J=139Hz)</td>
<td>6.67 - 7.75 (m, 22H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d,1H, J=142Hz)</td>
<td>6.67 - 7.75 (m, 22H)</td>
</tr>
<tr>
<td>Ph₃P</td>
<td>Ph₂P ClO₄</td>
<td>5.67 (d,1H, J=24Hz)</td>
<td>6.67 - 7.67 (m, 18H)</td>
</tr>
</tbody>
</table>

The effect resulted from the corresponding phosphonium salt would be expected less than that from the corresponding salt of triphenylphosphine. Therefore, it can be expected that this less induced magnetic effect, in turn, makes less downfield shift of a methine proton resolve to be able to see it as a doublet.

Besides chlorodiphenylphosphine, tribenzylphosphine was chosen in order to see whether or not phenyl groups of phosphonium salt from tribenzylphosphine have the same effect to the chemical shift as those of the corresponding salt from triphenylphosphine do. Surely delocalization of $d_π - p_π$ between phosphorus 3d orbitals and π orbitals of phenyl rings is prohibited in tribenzylphosphonium salt.

With these in mind, reactions with n-butylphosphine, tri-o-methoxyphenylphosphine, tribenzylphosphine, and chlorodiphenylphosphine were carried out in order to obtain the corresponding 9-thioxanthenylphosphonium salts. The following table (Table 1) compiles pmr data of the phosphonium salts except for one product.

**DISCUSSION**

In contrast with pmr spectrum of either triphenyl-9-thioxanthenylphosphonium or tri-o-methoxyphenyl-9-thioxanthenylphosphonium perchlorate, tri-n-butyl-9-thioxanthenylphosphonium perchlorate showed a doublet at δ 5.58, assigned to a methine proton (Fig. 1). This value is slightly larger than the corresponding values (5.0~5.2) of 9-arylthioxanthenes but clearly differentiated from those of aromatic protons. This result implies that the downfield shift of a methine proton signal of the compound to the aromatic region is not due to inductive effects of an electron deficient phosphorus atom but other effects arising from the groups on phosphorus atom.

Chemical shifts observed in organophosphorus compounds are quite sensitive to changes in molecular structure. Therefore, any attempt to interpret them in detail has been hopeless because of the number of intervening intra- or intermolecular contributions such as localized electronic charges, magnetically anisotropic heteroatoms or bonds, hydrogen bonding, and solute-solvent interaction. However, when discussing homologous series of parent compounds, the observed trends may be interpreted on the basis of inductive effects. In general, electronegative substituents make the phosphorus more positive and cause the proton resonance signals to be shifted downfield.
The chemical shift changes of substitution on methyl phosphonium CH₃P⁺R₃ are rather well correlated with inductive effects, as described by Taft's σ₁ or σ coefficients. However, irregularities appear when dealing with even the simplest nonhomologous series. This indicates that the contribution of d-orbitals, even if rather small, may be significant, especially through simple or double back-donation. All of these general properties have been obtained from the phosphonium salts bearing methyl, methylene, or vinyl group on phosphorus atom. However, little has been reported about the phosphonium salt having a methine group on phosphorus atom. Schweizer and Bach²⁷ reported pmr data of 1-phenoxyethyltriphenylphosphonium bromide; centered at δ 7.77, 7.33, and 7.04, two aromatic multiplets and a doublet somewhat overlapped, assigned to the phenoxy and triphenylphosphorus phenyls and the tertiary proton; centered at δ 1.76, a split doublet, assigned to the C-methyl protons. In this compound the methine proton signal was hidden with the aromatic proton signals. No explanation about this downfield shift of the methine proton signal was made.

Other example can be taken from Caesar and Balzer's report. Triphenyl-3-oxocyclohexylphosphonium chloride showed a multiplet at δ 7.82 ppm and a multiplet at δ 2.4 ppm, which were assigned to fifteen aromatic protons and eight methylene and one methine protons, respectively. It is uncertain why the methine proton signal appears at rather upfield in this compound since methylene protons on phosphorus atom of the phosphonium salt show a signal in the range of δ 3.6~6.3 ppm²⁷, 19-21.

Tri-o-methoxyphenyl-9-thioxanthene-9-phosphonium salt gave no resolved methine proton signal as in the triphenyl-9-thioxanthene-9-phosphonium salt, which means that electron-donating ability of methoxy groups is overshadowed by the other factors. Grim and co-worker²² studied ³¹P chemical shifts of triphenylphosphonium salts and obtained a straight line with the exception of phenyl by plotting group contribution to chemical shift of phosphonium salt vs the corresponding σ⁺ values. The deviation of phenyl from the straight line was reasoned by the fact that phenyl can act as a π-electron donor to the empty 3d orbitals of phosphorus in the

Fig. 1. Pmr spectra of (a) tri-o-methoxyphenyl-9-thioxanthene-9-phosphonium perchlorate, (b) tri-n-butyl-9-thioxanthene-9-phosphonium perchlorate, and (c) tribenzyl-9-thioxanthene-9-phosphonium perchlorate.
Phonium compounds. However, in our case, overlapping of a methine proton signal with the signals of aromatic protons suggests that the electron-donating effects of methoxy groups are not strong enough for shielding the phosphorus atom by contributing their nonbonding electrons to phenyl rings as \( \pi \)-electron donors.

On the other hand, chemical shift of a methine proton of tribenzyl-9-thioxanthenylphosphonium salt was almost the same as that of tri-\( n \)-butyl-9-thioxanthenylphosphonium salt. This result indicates the unimportant of phenyl groups when they are one carbon away from phosphorus and suggests that the conformation of three phenyl groups around phosphorus are important for the chemical shift of a methine proton. We propose that the ring current effect of three phenyl rings is a major cause for the downfield shift of a methine proton signal. If the phenyl groups are at a distance of one carbon away from the phosphorus atom, paramagnetic deshielding effect does not have influence on the methine proton and thus does not cause downfield shift of the methine proton signal. Therefore, benzyl groups act to the methine proton of the 9-thioxanthenylphosphonium salt exactly the same as the \( n \)-butyl groups do.

In order test further the involvement of paramagnetic deshielding effect by phenyl rings reaction with chlorodiphenylphosphine which had two phenyl groups was carried out. But the product obtained was diphenyl-9-thioxanthenylphosphine oxide rather than chlorodiphenyl-9-thioxanthenylphosphonium perchlorate. The formation of phosphine oxide can be explained by the Scheme 1.

In the case of the reaction with tripheny1phosphine, was obtained tripheny1phosphonium perchlorate, which decomposed to give thioanthenone and tripheny1phosphine oxide under rather drastic condition. The formation of tripheny1phosphine oxide seems to be reasonable because there is no good leaving group on phosphorus atom. By the same token, one can expect diphenyl-9-thioxanthenylphosphine oxide from chlorodiphenyl-9-thioxanthenylphosphonium perchlorate because chloride is believed to be a better leaving group than thioanthenone moiety.

We were unable to get pure chlorodiphenyl-9-thioxanthenylphosphonium perchlorate because of instability against water. But it seemed that acetone fraction obtained by column chromatography had initially the perchlorate, which then slowly decomposed to give diphenyl-9-thioxanthenylphosphine oxide. Evidence for the initial formation of chlorodiphenyl-9-thioxanthenylphosphonium perchlorate comes from the different eluting nature of the reaction mixtures. The phosphine oxide was very much insoluble in acetone or methanol. If the phosphine oxide had already formed during the course of the reaction, it would not be moved down by eluting with ether, acetone, or methanol as in the case of the reaction mixture treated with benzylamine in acetonitrile (vide supra). This indicates that in dry acetonitrile the corresponding phosphonium salt is presumably stable enough for being eluted.
with acetone without decomposition in column chromatography.

Purp spectrum of diphenyl-9-thioxanthenylphosphine oxide showed a methine proton signal at δ 5.1 ppm, smaller than δ 5.6 ppm of tri-n-butyl-9-thioxanthenylphosphonium perchlorate but very close to those of 9-aryltioxanthenes. Further study on the correlation of pmr data of the compounds structurally different is in progress.

**ACKNOWLEDGMENT**

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**REFERENCES**