Reactions of Thianthrene Cation radical Perchlorate with 1-Alkyl-4-Arenesulfonylaminobenzenes

Jae Sung Noh, So Ha Lee, and Kyongtae Kim

Department of Chemistry, Seoul National University, Seoul 151-741. Received February 1, 1988

Reactions of thianthrene cation radical perchlorate (1) with 1-methyl-4-benzenesulfonfylaminobenzene (10) afforded thianthrene (5), N-(4-toly)-N-thianthrenylbenzenesulfonamide (14), 1-methyl-3-[N-(4-toly)-N-benzenesulfonylamino-4-benzene-sulfonfylaminobenzene (16), cis-thianthrene-5,10-dioxide (17), 5-[3'-methyl-6-benzenesulfonfylaminobenzethianthrenium perchlorate (18), and benzenesulfonate. In the meantime, reaction of 1 with 1-ethyl-4-benzenesulfonfylaminobenzene (12) afforded 5, 1-ethyl-3-[N-(4-ethylphenyl)-N-benzenesulfonylamino-4-benzene-sulfonfylaminobenzene (19), 1-benzenesulfonfylamino-4-[1-(2-benzenesulfonfylaminophenyl)-ethyl]benzene (20), and 1-[1-acetamidoethyl]-4-benzenesulfonfylaminobenzene (21). The formations of these products except for 18 and benzenesulfonate could be rationalized by assuming a sulfonamidyl radical as an intermediate.

Introduction

Thianthrene cation radical perchlorate (1) is one of the most stable crystalline sulfur containing cation radical, so that reactions with 1 have been much exploited.1

We have previously reported the reactions of 1 with N-free sulfonamides (2) in which N-alkyl- or arylsulfonylsulfenamines (3) were obtained in good yields, although it took 3 months to observe complete discharge of dark purple color of 1 in acetonitrile (Scheme 1).

![Scheme 1](image)

N-Alkylsulfonamides (7), however, did not react with 1 and the unreacted sulfonamides were recovered quantitatively, along with the isolation of 4, 5, and 6 (Scheme 2).

![Scheme 2](image)

When N-arenesulfonamides (8) without having any substituent at para position of a N-aryl group2 were allowed to react with 1 at the same conditions as in the previous reactions foregoing, 5-(p-arenesulfonylamino-phenyl)thianthrenium perchlorates (9) were formed within an hour (Scheme 3).

Since benzene does not react with 1, one may realize that arenesulfonylamino groups activate the benzene ring. In order to see a substituent effect present at para position of a

Experimental

Materials and Apparatus. Thianthrene (5) was synthesized from the reaction of benzene and sulfur powder in the presence of anhydrous aluminum chloride according to the literature.4 Thianthrene cation radical perchlorate (1) was prepared by the method previously described.5 Acetonitrile was dried by refluxing over P2O5 for 3 h, followed by refluxing over calcium hydride and distilled twice. The distillate was stored over molecular sieve (4 Å) in a septum-capped bottle. All solvents used for the column chromatography were distilled before use.

Infrared spectra were recorded using a Perkin-Elmer model 283 infrared spectrometer.1H NMR spectra were obtained using a Varian EM 360A spectrometer and chemical shifts were represented in ppm relative to an internal standard (TMS). UV spectra were recorded on Beckman 5270 spectrometer. Melting points were measured using Fisher-Johns melting point apparatus and are not calibrated.

Thin layer chromatography was performed with Merck silica gel (Art. 7739) and the chromatogram was visualized by a mineral uv lamp. Column chromatography was carried out using Merck silica gel (Art. 7733). All solvents were specified in each case.

1) 1-Methyl-4-benzenesulfonfylaminobenzene (10). To a solution of 2.01 g (18.7 mmol) of p-toluidine in 50 ml of 10% potassium hydroxide was added 2.4 ml (18.8 mmol) of benzenesulfonfyl chloride. The mixture was stirred until the
odor of benzenesulfonyl chloride disappeared, followed by adjusting pH of the solution to be 4 using 25% aq. hydrochloric acid. Yield was 3.92 g (16.8 mmol, 96%); mp 123-123.5 °C (aq. ethanol) (lit. 123.1 °C); IR (KBr) 3320 (NH stre.), 1160 (SO₂ stre.) cm⁻¹. ¹H NMR (CDCl₃) δ 2.23 (s, 3H, CH₃), 7.00-7.35 (m, 10H, NH and aromatic).

(2) 1-Nitro-4-(p-toluenesulfonylamino)benzene (11). To a solution of 3.82 g (20.0 mmol) of p-toluenesulfonyl chloride and 2.73 g (19.5 mmol) of p-nitroaniline was added 5 ml of pyridine. The mixture was warmed for 20 min in an water bath, followed by washing with water. Dark yellow solid (4.77 g, 17.2 mmol, 86%) was decolorized and recrystallized from ethanol: mp 189-190 °C (lit. 191-192 °C); IR (KBr) 3220 (NH stre.), 1520, 1330 (SO₂ stre.), 1160 (SO₂ stre.) cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆) δ 2.39 (s, 3H, CH₃), 7.31-8.21 (m, 6H, aromatic), 10.40 (s, 1H, NH).

(3) 1-Ethyl-4-benzenesulfonylaminobenzene (12). To a solution of p-ethylaniline in 40 ml of pyridine was added the same number of moles of benzenesulfonyl chloride. The reaction mixture was allowed to stand at room temperature for 24 h. The red solution was poured to a large volume of an ice-water containing excess hydrochloric acid enough to neutralize the pyridine and allowed to stand overnight. The crude sulfonamide was filtered and washed with water, followed by dissolving in 5% NaOH solution. The sulfonamide was recovered by adding slowly hydrochloric acid with vigorous stirring until the solution was acidic to litmus paper. Recrystallization from aq. ethanol afforded a white needle type crystals: Yield 95%; mp 79.5-80 °C; ¹H NMR (CDCl₃) δ 1.14 (t, 3H, CH₃), 2.53 (q, 2H, CH₂), 6.90-7.20 (s, 4H, aromatic), 7.30-7.60 (m, 3H, aromatic), 7.70-8.00 (m, 3H, NH and aromatic); IR (KBr) 3200 (NH stre.) 1310 (SO₂ stre.), 1130 (SO₂ stre.) cm⁻¹.

(4) 1-Isopropyl-4-benzenesulfonylaminobenzene (13). Using the same procedure as described in (3), was obtained 95% yield of the desired compound: mp 110-110.5 °C (aq. ethanol); ¹H NMR (CDCl₃) δ 1.17 (d, 6H, 2CH₃), 2.90 (m, 1H, CH), 6.93-7.20 (s, 4H, aromatic), 7.53-7.68 (m, 4H, NH and aromatic), 7.68-8.00 (m, 2H, aromatic); IR (KBr) 3260 (NH stre.), 1150 (SO₂ stre.), 1330 (SO₂ stre.) cm⁻¹.

(5) Reaction of 1 with 1-Methyl-4-benzenesulfonylaminobenzene (10). To a stirred solution of 1.395 g (4.42 mmol) of 1 in 25 ml of acetonitrile was added 2.165 g (8.75 mmol) of 10. After the reaction flask was stoppered with a septum, stirring was continued until the color of 1 had completely disappeared. It took 13 days and the solution of the reaction mixture was dark green. The solvent was stripped off and the residue was extracted by adding chloroform (100 ml) and water (100 ml). The residue from chloroform layer was chromatographed on silica gel column (1.9 x 16 cm). Elution with hexane (50 ml x 5) gave 0.662 g (3.06 mmol) of 5, while elution with benzene (50 ml x 8) gave 0.827 g of a mixture with three components and 0.772 g (3.31 mmol) of 10. This mixture was rechromatographed on alumina(Merck active basic, Art. 1076, 1.9 x 12 cm) column. Elution with hexane (50 ml x 5) gave 0.07 g (0.36 mmol) of 5, while elution with benzene (50 ml x 4) gave 0.08 g (0.19 mmol) of a white solid, identified as N-(4-toly)-N-bianthrylenesulfonamide (14): mp 171-172 °C (aq, ethanol); λ_max (log ε) 264 (4.32), 243 (4.00) nm; ¹H NMR (CDCl₃) δ 2.31 (s, 3H, CH₃), 7.05-7.87 (m, 16H, aromatic); IR (KBr) 1165 (SO₂ stre.), 1350 (SO₂ stre.) cm⁻¹; MS, m/e (rel. intensity) 320(B), 461(44.3, M⁺). From the other benzene fraction was obtained 0.012 g (0.048 mmol) of thianthrene-5,5-dioxide (15): 168-169 °C (mp, aq, ethanol); IR (KBr) 1450, 1310 (SO₂ stre.), 1160 (SO₂ stre.) cm⁻¹. Elution with acetonitrile (50 ml x 4) gave 0.70 g of a mixture of 10 and one unknown compound, which was rechromatographed on alumina (Merck active acidic, Art 1078, 1.9 x 8 cm). Elution with benzene (50 ml x 4) gave 0.157 g (0.32 mmol) of a white solid, identified as 1-methyl-3-[N-(4-toly)-N-benzenesulfonyl]amino-4-benzenesulfonylaminobenzene (16): mp 108-109 °C (hexane-ethyl ether); ¹H NMR (CDCl₃, 100 MHz) δ 2.25 (s, 6H, 2CH₃), 6.85 (s, 1H, -NH), exchangeable in D₂O, 7.00-7.32 (m, 17H, aromatic); IR (KBr) 3250 (NH stre.), 1340 (SO₂ stre.), 1165 (SO₂ stre.) cm⁻¹. Elution with ether (50 ml x 5) gave 0.589 g (2.52 mmol) of 10 and 0.282 g of mixture of cis-thianthrene-5,10-dioxide (17) and a sticky material. Compound 17 was identified based on physical and spectral data: mp 247-248 °C (aq, ethanol) (lit. 249 °C); λ_max (nm) 210 nm; ¹H NMR (CDCl₃) δ 7.63-8.17 (m, aromatic), IR (KBr) 1080 (S = O stre.), 1020 (S = O stre.) cm⁻¹. Elution with acetonitrile gave 1.178 g of a dark brown sticky material from which 0.30 g of yellow solid was obtained by adding 1 ml of acetonitrile. Repeat of this treatment three times afforded 0.068 g (0.12 mmol) of yellow solid containing some brown materials, which was decolorized and then recrystallized from aq. ethanol to give pale yellow solid, identified as 5-(3-methyl-6-benzenesulfonylamino)thianthrene perchlorate (18): mp 168-169.5 °C; λ_max (nm) 222, 260, 315-320 (sh) nm; ¹H NMR (CDCl₃) δ 2.45 (s, 3H, CH₃), 6.62 (s, 1H, NH), 7.53-8.56 (m, 15H, aromatic), 8.56-9.13 (m, 2H, NH and aromatic); IR (KBr) 3261 (NH stre.), 1150 (SO₂ stre.), 1330 (SO₂ stre.) cm⁻¹.

(6) Reaction of 1 with 1-Nitro-4-(p-toluenesulfonyl-)amino)benzene (11). To a stirred solution of 1.053 g (3.33 mmol) of 1 in 45 ml of acetonitrile was added 2.395 g (8.64 mmol) of 11. This mixture was treated as in the reaction of 10 with 1. The color of the reaction mixture was pale red after 50 days stirring. Thin layer chromatography (Kiesel gel 60, F₂₅₄) with benzene showed four spots of which Rₙ values were 0.61, 0.33, 0.12 and 0, corresponding to 5, 6, 9, and an unknown, respectively. The reaction mixture was worked up and the residue was chromatographed on silica gel column (3.1 x 11 cm). Elution with hexane (50 ml x 9) gave 0.272 g (1.26 mmol) of 5, while elution with benzene (50 ml x 5) afforded 0.026 g (0.11 mmol) of 6. Elution with ether (50 ml x 13) gave 2.322 g (7.94 mmol) of 11. Finally elution with acetone (50 ml x 3) gave 1.103 g of dark brown sticky materials. Washing the materials with water gave 0.570 g of yellow solids, which were dissolved in a warm ethyl acetate. The ethyl acetate insoluble, white solid (0.239 g) was identified as 4 in view of physical and spectral data of the authentic sample.

(7) Reaction of 1 with 1-Ethyl-4-benzenesulfonylaminobenzene (12). To a stirred solution of 2.481 g (7.86 mmol) of 1 in 50 ml of dried acetonitrile was added 2.322 g (8.88 mmol) of 12 at room temperature. The reaction was completed in 7 days and the color of the reaction mixture became pale purple. The reaction mixture was worked up as
usual and the residue was chromatographed on silica gel column (4.5 x 5 cm). Elution with n-hexane (400 ml) gave 1.494 g (6.81 mmol) of 5, while elution with benzene (400 ml) gave a mixture of 0.50 g of unknown, showing two spots on tlc and 0.362 g (1.39 mmol) of 12. This mixture was rechromatographed on silica gel column (9.5 x 19 cm). From benzene fractions (200 ml) was obtained 0.122 g (0.23 mmol) of a white solid, identified as 1-ethyl-3[N-(4-ethylphenyl)-N-(benzenesulfonyl)]amino-4-benzenesulfonylaminobenzene (19); mp 103-103.5 °C (n-hexane-cyclohexane); UV λmaxCH3 272 (shoulder) nm; 1H NMR (CDCl3, 100 MHz) δ 1.08 (t, 6H, 2CH3), 2.47 (q, 4H, CH2), 6.84 (s, 1H, NH), 6.90-7.07 (m, 5H, aromatic), 7.22-7.58 (m, 8H, aromatic), 7.58-8.70 (m, 4H, aromatic); IR (KBr) 3290 (NH), 1353 (SO2 streut.), 1180 (SO2 streut.); Anal. Calcd. for C39H32N6O4S2: C, 67.22; H, 5.42; N, 5.38; O, 4.98; S, 11.37. Later benzene fractions (200 ml) gave 0.310 g (1.19 mmol) of 12. Elution of the original reaction mixture with methylene chloride (400 ml) gave 0.735 g of an unknown white solid: 1H NMR (CDCl3) δ 1.23 (q, 6H, 2CH3), 2.45 (q, 2H, CH2), 4.46 (q, 1H, CH), 6.56-6.78 (d, 3H, aromatic), 6.78-7.00 (s, 4H, aromatic), 7.18-7.50 (m, 10H, aromatic), 8.62 (1H, NH), 9.62 (1H, NH): IR (KBr) 3260 (NH streut.), 1340 (SO2 streut.), 1150 (SO2 streut.) cm⁻¹; Anal. Calcd. for C39H32N6O4S2: C, 64.59; H, 5.42; N, 5.38. Found: C, 64.43; H, 6.32; N, 5.21. Elution with acetone (100 ml) gave 1.51 g of a mixture with many spots on tlc. Repeated chromatography on silica gel using ethyl acetate gave 0.113 g (0.37 mmol) of a white solid, identified as 1-[(1-ethane-sulfonyl)amino-5-ethylphenyl]benzene (20): mp 206-206.5 °C; λmaxCH3 264 (shoulder), 272 (shoulder) nm; 1H NMR (CDCl3 + DMSO-d6) δ 1.22 (q, 6H, 2CH3), 2.45 (q, 2H, CH2), 4.46 (q, 1H, CH), 6.56-6.78 (d, 3H, aromatic), 6.78-7.00 (s, 4H, aromatic), 7.18-7.50 (m, 10H, aromatic), 8.62 (1H, NH), 9.62 (1H, NH): IR (KBr) 3260 (NH streut.), 1340 (SO2 streut.); Anal. Calcd. for C39H32N6O4S2: C, 64.59; H, 5.42; N, 5.38. Found: C, 64.43; H, 6.32; N, 5.21. Elution with acetone (100 ml) gave 1.51 g of a mixture with many spots on tlc.

**Results and Discussion**

(a) Reaction with 10

Reaction of 1 with 10 afforded several products as shown in Scheme 4.

![Scheme 4](image)

The numbers in the parenthesis represent millimoles of the reagents and the isolated products unless otherwise specified.

* Sticky materials included.

M is not identified.

**(8) Reaction of 1 with 1-isopropyl-4-benzenesulfonylaminobenzene (13).** To a stirred solution of 1.705 g (5.40 mmol) of 1 in 25 ml of anhydrous acetonitrile was added 2.646 g (9.61 mmol) of 13 at room temperature. The purple color of 1 turned blue in one day, followed by pale red in additional 2 days and finally colorless solution was obtained in additional 3 days. Tlc (benzene) of the reaction mixture showed four spots (Rf, 0.69, 0.49, 0.28, 0) corresponding to 5 (0.69), and 13 (0.28). However, tlc (CH3CN/CH2Cl2, 1/5, v/v) showed seven spots (Rf, 0.92, 0.90, 0.78, 0.21, 0.18, 0.14, 0.04). After the solvent was evaporated, in vacuo, the residue was chromatographed on silica gel column (1.5 x 10 cm). Elution with hexane (795 ml) gave 0.833 g (3.85 mmol) of 5, while elution with benzene (600 ml) gave 1.403 g of a mixture consisting of 13 as a major and an unknown as a minor. Elution was continually performed using chloroform, methylene chloride, acetone, and methanol. It was unsuccessful to purify any of these fractions. 1H NMR spectra of each fraction did not indicate the presence of an isopropyl group.

The structural assignment of 18, analogous to 9, was rather difficult because not only the yield was low but also it showed two sharp peaks due to perchlorate ion at 1120 and 1070 cm⁻¹ on its IR spectrum, which was prominently contrast with a broad, intense peak in the same region shown by many thianthrenium perchlorates. 10 But in connection with this research we studied the reaction of 1 with 21 and obtained analogous IR and 1H NMR spectra to those of 18.

The formation mechanism of 18 is uncertain. However, it can be explained by either a prior disproportionation or a half regeneration mechanism as in other cases. 10

The formation of 16 can be rationalized by a coupling reaction between two radical species (23a, 23b) which suggest that 10 is oxidized by 1 to form 1-methyl-4-benzenesulfonylaminobenzene cation radical (22) as shown in Scheme 5.
Reactions of Thianthrene Cation Radical

To our knowledge, chemistry of sulfonamide cation radical has not been reported although oxidations of some sulfonamides by the oxidants such as manganese dioxide and lead tetraacetate have been studied. Deprotonation of 22 gives rise to N-(p-tolyl)-benzenesulfonamidyl radical (23) which may be stabilized by resonance hybridizations. Sulfonamidyl radicals have been mainly generated by photolysis of N-halosulfonamide and oxidations of N-alkyl or -arylsulfonamides by sodium persulfate or hydrogen atom abstractions from N-monoalkylsulfonamides by t-butoxy radical also afforded the corresponding sulfonamidyl radicals. Of these works, there is only one report regarding the N-arylsulfonamidyl radical: [c, e] [1,2]thiazine 5,5-dioxide (25) was expected to be formed by way of 2-biphenylylsulfonamidyl radical (24) from the reaction of N-phenyl 2-biphenylylsulfonamide with sodium persulfate as shown in Scheme 6.

![Scheme 6](image)

Apart from the results from N-free and -alkyl analogs, only complex mixture was obtained. Therefore, isolation of 16 is the first demonstration of the product formed from N-arylsulfonamidyl radical.

The formation of 14 can be rationalized by a sulfonamidyl radical (23) substitution to 5 as in the formation mechanism of the sulfone in oxidation of biphenyl-2-sulfonylamines.

We do not know the substitution position of thianthrene moiety to which radical 23 is bonded. However, we prefer the structure represented by 14 simply because a large steric hindrance is expected to be avoided at 2 position of thianthrene ring as shown in Scheme 7.

![Scheme 7](image)

One may speculate the combination reaction between 1 and 23a to lead 14 as shown in Scheme 8.

![Scheme 8](image)

This possibility, at present moment, cannot be excluded for the formation mechanism of 14.

The formation of thianthrene 5,5-dioxide (15) and cis-thianthrene-5,10-dioxide (17) suggest also the involvement of a peroxy radical as we have previously proposed in the reactions of 1 with dibutyl peroxide, azo-bis-isobutyronitrile, acetyl cyanide, and azo-bis-2-phenoxy-2-propane. We believe that compounds 15 and 17 are not formed in the reactions in which no peroxy radical is produced during the course of the reaction. Therefore, Scheme 9 is proposed for the formation mechanisms of 15 and 17.

![Scheme 9](image)

Thianthrenesulfinyl oxide (27) was proposed as an intermediate in the reaction of 1 with superoxide. Ando et al. did not obtain 15 and 17. Originally Foces et al. proposed sulfinyl oxide as an intermediate in the photooxidation of sulfides by singlet oxygen from which sulfite, sulfone, and sulfide were obtained and the yield of each product varied depending on the reaction conditions. Hence the fact that Ando et al. did not detect 15 and 17 in their reaction is not unexpected. Since 1 does not react with triplet oxygen, the formation of 27 can be explained by assuming an intermediate, 26, which, to our knowledge, has not been reported. However, one report shows that sulfonamidyl radical behaves usually in the presence of oxygen. That is, Neale et al. generated N-methylmethanesulfonamidyl radical by photolysis of the corresponding N-chloro compound. The sulfonamidyl radical added to styrene but no addition product was obtained in the presence of oxygen. This result indicates that trapping of the sulfonamidyl radical by oxygen is faster than the addition reaction. Therefore, the assumption of peroxy radical, 26, is reasonable.

(b) Reaction with 12

The results are summarized in Scheme 10.

![Scheme 10](image)

Compounds 19 is analogous to compound 16, which are identified by NH stretching band at 3290 cm⁻¹ and a singlet corresponding to one proton at 6.84 ppm, exchangeable with D₂O. Compounds 20 and 21 are compounds which are not produced in the reaction of 1 with 10. The structure of 21 was identified by the spectral data and an elemental analysis (vide supra) as well as comparison with those of the authentic sample. Since acetamido group of 21 is thought to be from
acetonitrile, one may think generation of benzylic cation (32) as shown in Scheme 11 via oxidation and a series of protonation-deprotonation processes.

\[
\begin{align*}
1 + 12 & \rightarrow 5 + \text{CH}_2 \text{CH}_2 \text{Cl}^+ \\
28 & \\
29c & \rightarrow \text{SO}_2 \text{N} = \text{CN} = \text{CH}_2 \text{Cl}^+ \\
29d & \\
29 + 1 & \rightarrow 5 + \text{CH}_2 \text{Cl} \text{CH}_2 \text{Cl}^+ \\
30c & \\
30b & \\
30a & \\
30 & \\
30c & \\
31 & \\
32 & \\
33 & \\
34 &
\end{align*}
\]

**Scheme 11**

It is unlikely that 30 is directly generated from 28 by loss of a hydrogen atom. In such a case, only one mole of 1 is used for the reaction of one mole of 12 through the reaction. Since 1.23 g of unknown compounds are thought to be originated from 12 in view of \(^1H\) NMR and IR data, relatively small amounts of 12 are expected to be remaindered. On the other hand, two moles of 1 should be used for one mole of 12 according to Scheme 11. Therefore, unreacted 12 should be twice greater in the latter than in the former. The experimental result in which 2.58 mmol of 12 is recovered is more consistent with the latter than the former.

The intermediacy of 31 in Scheme 11 is interesting because this type of benzenesulfonylamine has not been prepared although quinone imides have been attracted much attention. 12,20,21

The formation of 20 can also be explained by an electrophilic substitution of 32 to 12. Reaction of 1 with 10 does not give the analogous compounds to 20 and 21. This difference between two analogs, 10 and 12, may be due to the stability of the corresponding intermediates, 33 and 31, in which 31 is more stable than 33.

(c) **Reaction with 13**

Apart from the reactions with 10 and 12, this reaction gave very complicated reaction mixture from which only 5 and unreacted 13 were identified. Compound 5 is normally eluted from n-hexane or benzene. So sufficient amounts of these solvents were used to remove 5 but even acetone fractions showed the presence of 5. This compound indicates that acetone fraction has unknown compound(s) containing thianthrene moiety, which decompose(s) during the process of chromatography. \(^1H\) NMR (CDCl\(_3\) + DMSO-d\(_6\)) of acetone fraction showed a doublet at 1.2 ppm, a singlet at 2.15 ppm, a singlet at 2.65 ppm, and a multiplet at 7.69 to 8.3 ppm. Attempted recrystallizations of acetone fractions from various solvents were unsuccessful. Treatment with 5% aq. NaOH, followed by refluxing afforded also 5 and several unidentified products. Chloroform, methylene chloride, and methanol fractions gave products, which did not show the presence of isopropyl group on \(^1H\) NMR spectra.

By the analogy with an intermediate, 31, 34 is expected to be formed readily, compared with 31 but in this case deisopropylation seems to be a facile reaction.

In conclusion, reactions of 1 with 1-alkyl-4-benzenesulfonylamino-benzenes are sensitive to the nature of alkyl groups. Further investigations of these reactions are in progress.

**Acknowledgement.** The authors gratefully acknowledge the financial support of Korea Research Foundation in this work.

**References and Notes**


11. Compound 21 was prepared via an independent route and a reaction of 21 with 1 was investigated. From this reaction was obtained a compound in good yield of which structure was assigned to be 35 based on spectral data and the result of an elemental analysis. IR of this compound showed two sharp peaks at 1120 and 1070 cm\(^{-1}\) and \(^1H\) NMR spectrum showed the same type of peaks as that obtained from 18 between 6.5 and 9.0 ppm.
A Stirereoselective Synthesis of (Z,Z)-3,13-Octadecadien-1-yl Acetate, and Its (E,Z)-Isomer, the Sex Pheromone of the Cherry Tree Borer, Synanthedon hector Butler

Suk-Ku Kang* and Sun-Ku Park

Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 440-746
Received February 2, 1988

A mixture of (Z,Z)-3,13-octadecadien-1-yl acetate(1) and its (E,Z)-isomer(2), the sex pheromone of the cherry tree borer, Synanthedon hector Butler was synthesized. (Z)-11-Octadecen-1-ol(3) was prepared from 1,10-decadiol. The Wittig reaction of the above aldehyde3 with carboxethoxyethylmethyltriphosphonoacetate, or the Wadsworth-Emmons reaction of the above aldehyde3 with the anion of triethylphosphonoacetate gave ethyl (Z,Z)-2,13-octadecadienoate and its (E,Z)-isomer. Deconjugative protonation of ethyl (Z,Z)-2,13-octadecadienoate and its (E,Z)-isomer with potassium hexamethyldisilazide followed by aqueous ammonium chloride work-up afforded stereoselectively ethyl (E,Z)-3,13-octadecadienoate and its (Z,Z)-isomer, respectively, of which stereoselectivity was adjusted to give the product in the required ratio. Exposure of the above deconjugated ester to excess lithium aluminium hydride resulted in formation of the penultimate (Z,Z)-3,13-octadecadien-1-yl and its (Z,Z)-isomer. Acetylation of the desired alcohols afforded the final products, (Z,Z)-3,13-octadecadien-1-yl acetate(1) and its (E,Z)-isomer(2).

Introduction

The sex pheromone of the cherry tree borer, Synanthedon hector Butler, was isolated and identified as a mixture of (Z,Z)-3,13-octadecadien-1-yl acetate(1) and its (E,Z)-isomer(2) (Figure 1) by Yaginuma et al.1 and Voerman et al.2 The cherry tree borer, Synanthedon hector Butler, is one of the most important pests of peach and various deciduous fruit trees in Korea3 and Japan4. Also sex pheromones of the less peach tree borer, Synanthedon pictipes5 Grote Robinson and the peach tree borer, Synninorinae eversa5 Say were identified as (Z,Z)-3,13-octadecadien-1-yl acetate(1) and its (E,Z)-isomer(2).

Generally, Synanthedon species (Lepidoptera: Sesidae) were found to be attracted by a mixture of the (Z,Z)-isomer 1 and the (E,Z)-isomer 2, which suggest that relatively low species-specificity of the pheromone component of Sesidae. Recently, the highly purified (Z,Z)-isomer 1 was shown to be attractive to the smaller clear wing, Synanthedon tenax6, which is the pest in Japanese persimmon orchards. Even 0.5% contamination of the (E,Z)-isomer 2 inhibited6 the attractancy of the (Z,Z)-isomer 1.

Several syntheses7 of the (Z,Z)-isomer 1 and the (E,Z)-isomer have been reported in the literature.

A mixture (1:1) of the (Z,Z)-isomer 1 and the (E,Z)-isomer 2 was known to be an effective trap bait for the male cherry tree borer, an economic pest in Korean peach orchards. We have devised a convenient synthesis of the mixture of the (Z,Z)-isomer 1 and the (E,Z)-isomer 2 employing the Wittig or Emmons reaction followed by deconjugative protonation as the key step, which were adjusted to give the products in the required ratio.

Figure 1