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Photoreaction of 1,6-Disubstituted-1,3,5-hexatriynes with Some Olefins

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When the two conjugated poly-ynes, 1-phenyl-6-methyl- and 1,6-diphenyl-1,3,5-hexatriynes, were irradiated with UVA in deaerated 2,3-dimethyl-2-butene solution, 1:2 photoadducts, 1-(1'-phenylethynyl-2',2',3',3'-tetramethylcyclopropyl)-2-(1",2",2",3",3"-pentamethylcyclopropyl) acetylene and 1-(1'- phenylethynyl-2',2',3',3' -tetramethylcyclopropyl)-2-(1"-phenyl-2",2",3",3"-tetramethylcyclopropyl) acetylene, were obtained, respectively. No photoadduct was formed with aerated 2,3-dimethyl-2-butene, or deaerated solutions of dimethyl fumarate, methyl crotonate, dimethyl maleate, and trans-1,2-dichloroethylene. The results suggest that the reactions proceed from the triplet state only with electron rich olefins such as 2,3-dimethyl-2-butene.

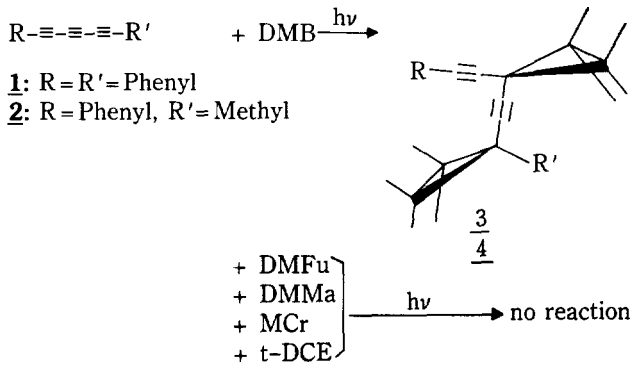
Introduction

A naturally occurring conjugated polyacetylene, 1-phenyl-1,3,5-heptatriyne (PHT), is phototoxic to a variety of micro organisms, bacteriophages, animal viruses, human erythrocytes, algae, nematodes, cercariae, and the larvae.[1-10] Previous report shows that the phototoxicity of PHT exerts influence to viruses but only to those with membranes.[10] It was also reported that murine cytomegalovirus, which has been rendered non-infectious by treatment with PHT-UVA, is incapable of synthesizing viral DNA and viral RNA and proteins, in spite of the fact that the treated viral genome and virion proteins can penetrate susceptible cells and nuclei in a normal manner.[11] Furthermore the viral genome remains essentially intact and no cross-links formation is observed but the base sensitive cross-links such as protein-DNA etc. are not ruled out because cross-links were tested through the treatment of base. It was reported previously that PHT can produce PHT radical cation and anion via one electron transfer reaction with electron donor or acceptor such as methylviologen(electron acceptor) or triethylamine(electron donor).[12] In addition it was suggested that PHT radical cation is likely to be the phototoxic species responsible for the non-oxidative process. Until now, however, no information on photoreactions of PHT and reactive site for phototoxicity is available. For this reason, the photoreaction of 1,6-diphenyl-1,3,5-hexatriyne (DPH) and PHT with some olefins are investigated as a model reaction for the PHT phototoxicity and to elucidate the molecular mechanism for the PHT phototoxicity.

Results and Discussion

Photoreaction of PHT and DPH with some olefins. PHT and DPH were photolyzed in deaerated solutions of several olefins. No photoproduct was obtained from dimethyl fumarate, methyl crotonate, dimethyl maleate, and *trans*-1,2-dichloroethylene while 1:2 photoadducts were obtained

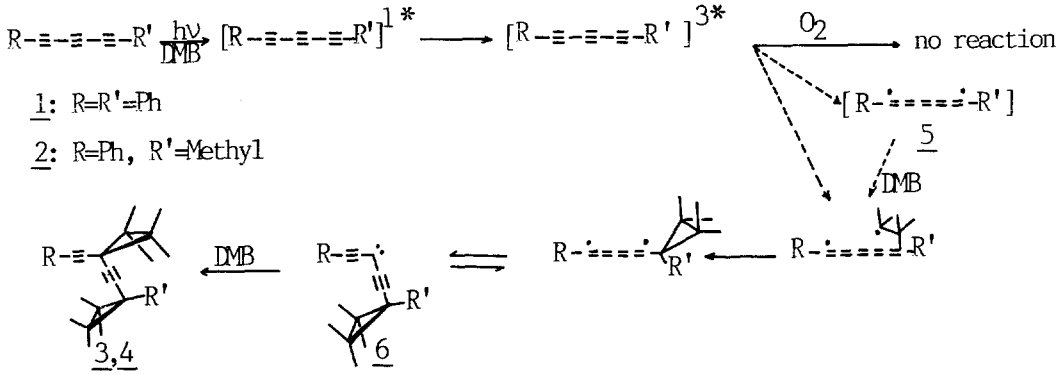
with deaerated DMB solution. The structure of these photoadducts were determined by various spectral data.



DMB: 2,3-dimethyl-2-butene, DMFu: dimethyl fumarate, DMMa: dimethyl maleate, MCR: methyl crotonate, t-DCE: trans-1,2-dichloroethylene.

When deaerated DMB solution of DPH is irradiated with 350 nm UV light, 1-(1'-phenylethynyl-2',2',3',3'-tetramethylcyclopropyl)-2-(1"-phenyl-2",2",3",3"-tetramethylcyclopropyl) acetylene(**3**) is obtained in 33% yield as a major product while 1-(1'-phenylethynyl-2',2',3',3'-tetramethylcyclopropyl)-2-(1",2",2",3",3"-pentamethylcyclopropyl) acetylene (**4**) is obtained in 11% yield along with minor side products from **2**. The residues are identified as colored polymers. When aerated DMB solution of **1** and **2** were irradiated with 350 nm UV light, no photoproduct was observed with most of the reactant recovered.

Since the triplet states of these molecules are efficiently quenched by O_2, the results indicate that the photoadducts, **3** and **4**, are originated from the triplet state of DPH and PHT. Oxygen quenches the triplet state of PHT with a rate constant of $1.7 \times 10^9\ M^{-1}\ s^{-1}$ to generate singlet oxygen.[12] Since DMFu, MCr, DMMa, and t-DCE which are electron deficient olefins do not give any photoproduct, it is clear that the



Scheme 1. A plausible reaction mechanism for **1** and **2**-DMB photoaddition reaction.

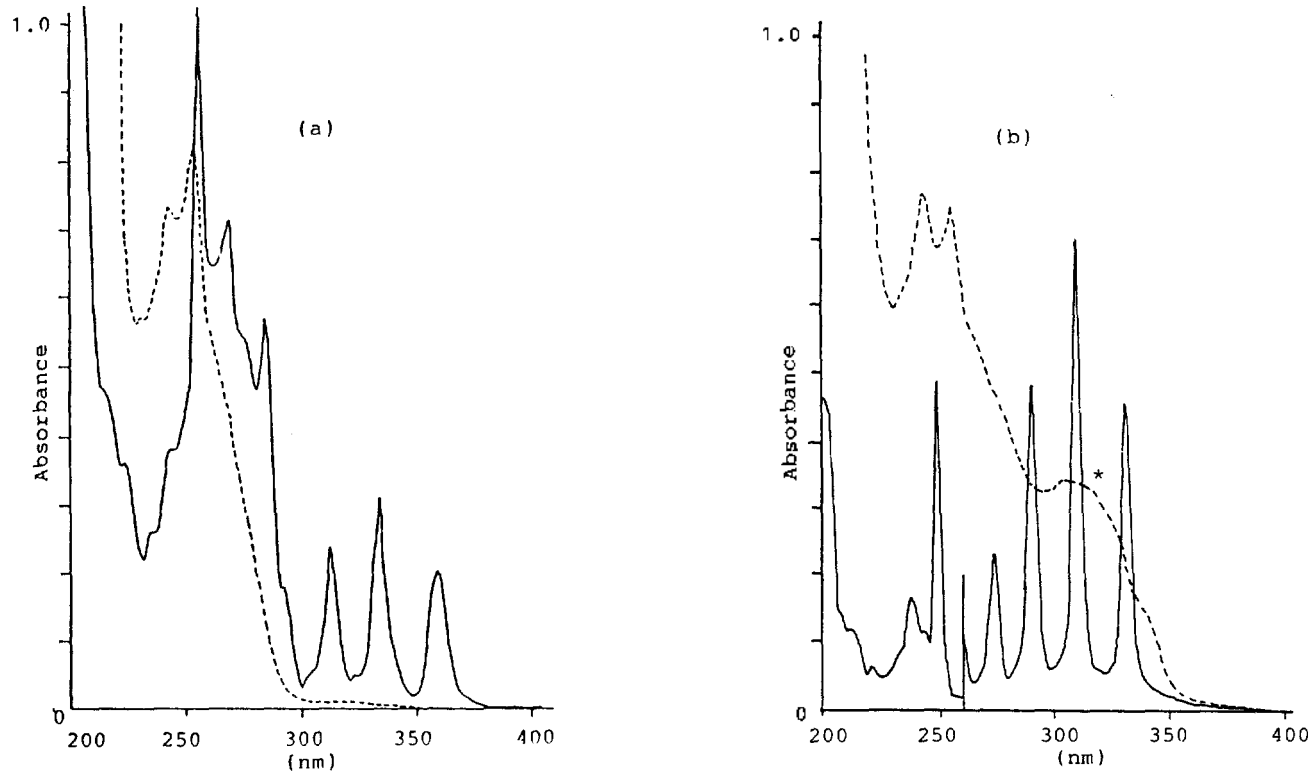


Figure 1. Ultraviolet absorption spectra of (a) DPH(**1**) (—) and photoadduct(**3**) (--) in MeOH. (b) PHT(**2**) (—) and photoadduct (**4**) (--) in MeOH. (*impurity).

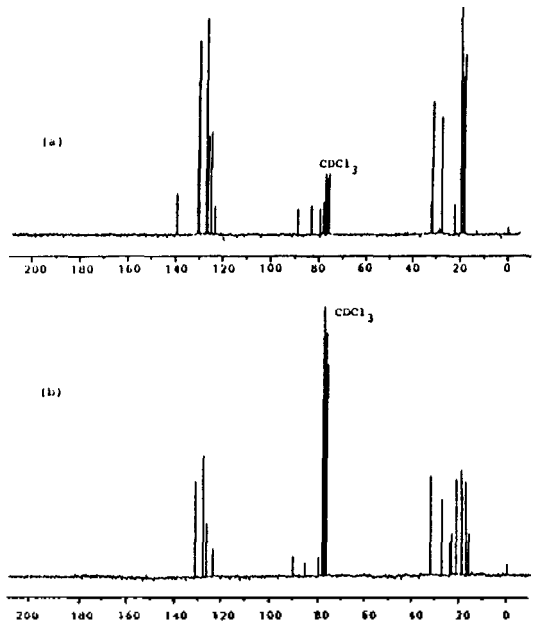


Figure 2. (2) ^{13}C NMR spectrum of **3** in $CDCl_3$. (b) ^{13}C NMR spectrum of **4** in $CDCl_3$.

photoaddition reaction of PHT and DPH with olefins requires electron rich olefins.

Structure determination of photoadducts. Conjugated poly-ynes exhibit characteristic electronic absorption spectra with the most prominent feature being a very high intensity band with well defined vibrational fine structure. The photoadducts **3** and **4** do not exhibit these typical poly-yne bands and absorption maxima are blue-shifted. In addition, the UV spectra are similar to those of phenylacetylenes as shown in Figure 1.

These spectra exhibit the interruption of conjugation in the system and indicate the presence of phenylacetylene moiety. IR spectra of these photoadducts reveal a low intensity peak at 2240 cm^{-1} which also indicates the interruption of conjugation in the products. From the mass spectra, M^+, M^+-DMB, and M^+-2DMB peaks are identified. The results indicate that photoadducts are formed by adding 2 molecules of DMB to 1,6-disubstituted-1,3,5-hexatriynes.

The ^{13}C NMR spectra shown in Figure 2 indicate the reaction sites and the structure of photoadducts which explain the reaction mechanism.

Figure 2(a) shows the four sp hybridized carbons and two kinds of substituted phenyl ring carbons. The peaks at 140.22 and 124.22 ppm reveal that the substituents are cyclopropane and ethynyl group by the additive rule of ^{13}C chemical shift, respectively. The remaining eight ring carbons of two phenyl groups appear as six peaks and eight alkyl carbons of 14 alkyl carbon chain are shown in the region of 18-32 ppm because of their symmetry.

In the Figure 2(b) four sp hybridized carbon peaks and four phenyl carbon peaks are shown and nine alkyl peaks are observed in the region of 16-33 ppm. In particular, the peak at 124.26 ppm and disappearance of the peak at 4.8 ppm support the structure of **4**. Two cyclopropane rings are formed at 3 and 6-positions of **1** as a result of the addition of two DMB molecules. The photoproduct **4** is obtained as a result of addition of two DMB molecules to **2**.

Mechanism of the photoaddition reaction. **1** and **2** are photolyzed with several olefins, electron rich and electron poor, and their reactivity is compared. The electron rich olefin, DMB, gave photoproducts **3** and **4**, respectively while no photoproduct was obtained from aerated DMB solution suggesting the triplet reaction mechanism for photoaddition reaction of **1** and **2** with DMB. It was reported that the triplet state of PHT was efficiently quenched by oxygen or by a good electron acceptor such as methylviologen, with almost diffusion controlled rates. The triplet state quenching by O_2 leads to type II mechanism by the formation of singlet oxygen but the triplet state quenching by good electron acceptor such as methylviologen leads to the non-oxidative toxic mechanism by the formation of semioxidized PHT radical.[12] The results obtained from the photoreaction of PHT with olefins cannot be explained by the formation of semioxidized PHT radical. If the reactions proceed via radicl cation of PHT, the reactions may be more favorable with the electron deficient olefins because electron affinity of electron deficient olefins is higher than that of electron rich olefins. In contrast to this expectation, they are inactive to the electron deficient olefins and photoreact only with electron rich olefins. The structure of the isolated photoadducts show that DMB was directly added to the triplet state of **1** and **2** and strongly support the existence of two reactive sites. A plausible reaction mechanism on the photoaddition reaction of **1** and **2** with DMB is shown in Scheme 1. Two reactive sites at 3 and 6-positions in **2** can be justified by the resonance structure of cummulene type diradical species, **5**, which supports the triplet mechanism because the triplet diradicaloids favor the geometry in which the free(radical) valences are as far apart as possible.[13] DMB reacts first at 6-position because the radical formed at 1-position is better stabilized by phenyl group compared to the radical formed at 6-position. The first addition of DMB molecule to **5** at 6-position probably generates carbene, **6**, at 3-position which attacks the second DMB molecule.

The photoreaction of **1** and **2** with DMB is the first photochemical model reaction to reveal the photochemical reactivity of PHT with substrates in vivo or vitro, and also the results show the distinct difference from the photochemical reactivities of α-naphthyl containing 1,3,5-hexatriynes and aryl containing 1,3-butadiynes.[14] The study of another conjugated poly-ynes, α-naphthyl containing 1,3,5-hexatriynes and aryl containing 1,3-butadiynes, show very different photochemical reactivity from PHT or DPH. No cyclopropane photoadduct was obtained with deaerated DMB solution. In addition, aryl containing 1,3-butadiynes undergo the photocatalyzed alcohol addition reaction while PHT and DPH are considerably stable in alcohol on irradiation. The photoaddition reaction which form the two cyclopropane rings is, therefore, a unique photoreaction of PHT type compounds and phototoxicity of PHT may be originated from this type of photoreaction.

Experimental

Instruments. ^1H-Nuclear magnetic resonance spectra were run in $CDCl_3$ on a Varian T-60A, FT-80A, and Bruker AM-200-SY spectrometers. Infrared spectra were obtained on a Perkin-Elmer 283B spectrophotometer in KBr pellets and NaCl cell. UV-VIS spectra were recorded on a Cary-17 spectrophotometer. Mass spectra were determined at 70 eV

with a Hewlett Packard 5985A GC/MS system by electron impact method.

Materials. Phenylacetylene, trimethylisilyl chloride, (Z)-1-methoxybut-1-en-3-yne were purchased from Fluka and were used without further purification and (Z)-1-methoxybut-1-en-3-yne was purified according to the literature procedure prior to use.[14] Methyliodide, n-butyllithium(1.6 M hexane solution), iodobezene, 2,3-dimethyl-2-butene were purchased from Aldrich Chemical Co. and were used as received. Extra pure solvents were used as received or after purification by distillation or by the standard methods.[16] Column chromatography was performed by using Kiesel gel 60(Merck, 70-230 mesh and 230-400 mesh). Preparative thin layer chromatography was conducted using Kiesel gel 60 GF_{254} (Merck) containing a fluorescent indicator.

Bromophenylacetylene(7) was prepared by the reported method.[17]

1-Trimethylsilyl-1,3-pentadiyne(8). A solution of (Z)-1-methoxybut-1-en-3-yne(30 mmol) in THF(60 ml) was treated with n-BuLi(30 mmol) at −78°C followed by Me_3SiCl(32 mmol). The mixture was warmed to 0°C and stirred for 2 hr. **8** was prepared by sequential treatment of the mixture at −40 ∼ −45 °C with n-BuLi(60 mmol) for 30 min followed by CH_3I(62 mmol). The resulting reaction mixture was warmed to room temperature and stirred for 2 hr. After then, the reaction mixture was extracted by n-pentane to give **8**. Yield: 80% ^{1}H NMR($CDCl_3$) δ 1.86(s,3H) 0.1(s,9H); IR(NaCl) 2950, 2260, 2140, 1420, 1260, 1210, and 860 cm^{-1}; MS, m/e 136(M^+, 13.2), 121(M^+-CH_3, 100).

1-Trimethylsilyl-1,3-butadiyne(9) was prepared by the same procedure used for **8**. Two equivalents of n-BuLi were added to reaction mixture treated by Me_3SiCl at −40∼−45°C in the period of 30 min. In this step, the reaction mixture was treated with aqueous hydrochloric acid to give **9**. Crude product was purified by column chromatography using petroleum ether as an eluting solvent. Yield: 80% ^{1}H NMR($CDCl_3$) δ 2.2(s,1H), 0.4(s,9H); IR(NaCl) 3310, 2940, 2180, 2150, 1460, 1390, and 840 cm^{-1}; MS, m/e 122(M^+, 14.5), 107(M^+-CH_3, 11.6), 73($C_3H_9Si^+$,100).

1-Trimethylsilyl-4-phenyl-1,3-butadiyne (10). To a mixture of 1-trimethylsilyl-1,3-butadiyne(**9**, 4.88 g, 40 mmol) and iodobezene(8.16 g, 40 mmol) in deaerated anhydrous triethylamine(120 ml) were added bis[triphenylphosphine] palladium dichloride(700 mg, 1 mmol) and copper (I) iodide(50 mg, 0.5 mmol). The reaction mixture is stirred at 30°C for 40 min under nitrogen and then the solvent is removed under the reduced pressure. The residue is extracted into petroleum ether followed by decolourization with activated charcoal and purified by chromatography on silica gel using petroleum ether as an eluent. Yield: 72% ^{1}H NMR($CDCl_3$) δ 7.1(m,5H), 0.1(s,9H); ^{13}C NMR($CDCl_3$) δ 133, 129.8, 129, 121.8, 90.5, 88.5, 77, 74.8, 0; IR(NaCl) 3080, 2980, 2220, 2120, 1620, 1580, 1500, 1450, 1260, 860, 760, and 690 cm^{-1}; UV(methanol) λmax 297, 279, 263, 250, 229, and 215 nm; MS, m/e 198(M^+, 32.0), 183(M^+-CH_3,100).

1-Phenyl-1,3,5-heptatriyne(2). A solution of **8**(2.72 g, 20 mmol) in methanol(5 m*l*) was treated with 30 m*l* of 1N-NaOH(in MeOH) at room temperature. After 10 min the solution was treated with 6 m*l* of 5N-HCl(in MeOH). The resulting NaCl was filtered and CuCl(0.2 g, 2 mmol), $NH_2OH\cdot HCl$(0.2 g, 2.8 mmol), and 70% $EtNH_2$ (4 m*l*, 50 mmol) were added to the filtrate. Bromophenylacetylene(**7**, 3.62 g, 20 mmol) in MeOH(20 m*l*) was added dropwise in 15 min and the mixture was stirred at 20°C for 1 hr under nitrogen, acidified, and extracted with n-pentane. The n-pentane extracts were dried and the solvent was removed under reduced pressure and the residue was crystallized to give **2**. Yield: 65% ^{1}H NMR($CDCl_3$) δ 7.3(m,5H),2(s,3H); ^{13}C NMR($CDCl_3$) δ 133, 130, 129, 120.4, 79, 75.7, 75, 68, 65.4, 59.5, 4.8; IR(NaCl) 3080, 2940, 2240, 1600, 1500, 1450, 1380, 760, and 690 cm^{-1}; UV(methanol) λmax 330, 309, 289, 273, 249, and 237 nm; MS, m/e 164 (M^+,100), 153(M^+-H,51).

1,6-Diphenyl-1,3,5-hexatriyne(1). Exactly the same procedure used for the preparation of **2** was followed starting with a solution of **10**(3.96 g, 20 mmol) in methanol(5 m*l*) to obtain **1** in 55% yield. ^{1}H NMR ($CDCl_3$) δ 7.4(m,10H); ^{13}C NMR ($CDCl_3$) δ 134, 131, 130, 122, 80, 76, 68; IR(NaCl) 3080, 2260, 2200, 1600, 1585, 1505, 1450, 910, 755, and 687 cm^{-1}; UV(methanol) λmax 358, 332, 311, 283, 267, 254 nm; MS, m/e 226(M^+,100).

Irradiation of 1 with DMB. Deaerated 4 mM DMB solution of **1** was irradiated with 350 nm UV light in a Rayonet Photochemical Reactor Model RPR-208 equipped with RUL-3500 Å lamps. After the irradiation for 48 hr, the resulting photoreaction mixture was concentrated in vacuo. The photoadduct, **3**, was isolated by column chromatography using n-pentane as eluting solvent. Yield: 33% ^{1}H NMR ($CDCl_3$) δ 1.3(s,6H), 1.1(s,6H), 1.0(s,6H), 0.9(s,6H), 7.2 (m,10H); ^{13}C NMR($CDCl_3$) δ 140.22, 131.55, 131.07, 128.04, 127.93, 127.25, 125.99, 124.22, 89.65, 84.00, 80.15, 78.65, 32.96, 32.52, 30.69, 28.69, 23.22, 20.63, 20.55, 19.28, 19.7; IR(NaCl) 3020, 2940, 2240, 1630, 1500, 1460, 1390, 760, 710, and 695 cm^{-1}; UV(methanol) λmax 253,242 nm; MS, m/e 394(M^+,8.6), 379(M^+-CH_3,7.1), 310(M^+-DMB,100), 226(M^+-2DMB,41.4).

Irradiation of 2 with DMB. Deaerated 4 mM DMB solution of **2** was irradiated as described. After the irradiation for 48 hr, the resulting photoreaction mixture was concentrated in vacuo. The photoadduct, **4**, was isolated by preparative thin layer chromatography using n-pentane-diethyl ether(20:1) followed by column chromatography using n-pentane as an eluent. Yield: 11% ^{1}H NMR($CDCl_3$) δ 7.3(m,5H), [1.32(s), 1.3(s), 1.23(s), 1.07(s), 27H]; ^{13}C NMR($CDCl_3$) δ 131.62, 128.05, 127.28, 124.26, 89.86, 85.31, 80.16, 76.75, 32.23, 26.02, 23.80, 22.80, 20.51, 19.40, 19.33, 17.49, 16.10; IR(NaCl) 3080, 3020, 2940, 2240, 1610, 1500, 1450, 1390, 1100, 760, and 690 cm^{-1}; UV(methanol) λmax 305, 252, 240 nm; MS, m/e 332(M^+, 36.5), 317(M^+-CH_3,76), 248(M^+- DMB, 8.3), 164(M^+-2DMB,90.1).

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A Chiral Synthesis of a Mosquito Oviposition Pheromone

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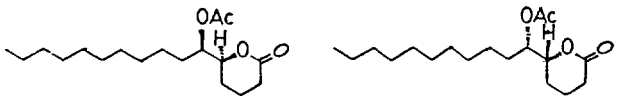
(+)-(5S,6R)-Erythro-6-acetoxy-5-hexadecanolide, an optically active form of them ajor component of an oviposition attractant pheromone of a mosquito **Culex pipiens fatigans**, was synthesized enantiospecifically from (−)-2-deoxy-D-ribose.

Introduction

Recently great advances have been made in total synthesis of optically active natural products from readily available chiral precursors such as carbohydrates, amino acids, hydroxy acids, and terpenes.[1]

Since the absolute stereochemistry of pheromones is important in pheromone activity, a number of chiral pheromones have been synthesized from chiral pools.[2] As a part of our research program directed toward the synthesis of chiral pheromones, we wish to describe a chiral synthesis of (+)-(5S,6R)-erythro-6-acetoxy-5-hexadecanolide, an optically active form of the major component of a mosquito oviposition attractant pheromone.

The oviposition attractant pheromone of the mosquito **Culex pipiens fatigans** was isolated from the optical droplet of the mosquito eggs and identified erythro-6-acetoxy-5-hexadecanolide by Laurence and Pickett.[3]The synthetic racemate(*la*→*lb*) (Figure 1) was reported as active as the natural pheromone. K. Machiya[4] tested the bioassay of the four erythro-and threo-isomers and reported that(−)-(5R,6S)-erytro-6-acetoxy-5-hexadecanolide was the most effective as an attractant. Recently B.R. Laurence and K. Mori[5] reported that (−)-(5R,6S)-(lb) enantioner is the vioposition attractant pheromone and the more biologically active enantiomer.



la lb

Several syntheses of erythro-6-acetoxy-5-hexadecanolide have been reported in the literature. C. Fuganti,[6] K. Mori,[7] and T. Fujisawa[8] have reported the synthesis of both enantiomers. One enantiomer(**la**) was synthesized from (+)-diethyl tartrate by Y. Masaki.[9] L. Gue-qiang[10] and K. Machiva[4] reported the synthesis of the four optical isomers of the mosquito oviposition attractant pheromone.

Results and Discussion

By retrosynthetic analysis, 2-deoxy-D-ribose(**2**) can be manipulated to (5S,6R)-erythro-6-acetoxy-5-hexadecanolide (**la**), in which the original chiral centers(5S,6R) of 2-deoxy-D-ribose is preserved without racemization (Scheme 1).

The C(3)-C(7) segment for the establishment of **la** is 2-deoxy-D-ribose.[11] The segment C(1)-C(2) can be constructed by the Wittig coupling of 2-deoxy-D-ribose with [(ethoxycarbonyl)methylene]triphenylphosphorane. One the other hand, the fragment C(8)-C(16) can be also constructed