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Synthesis and Biological Test of the Pheromone of the Asian Corn Borer Moth (*Ostrina Furnacalis*)

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(Z)-12-Tetradecen-1-yl acetate (**1**), (E)-12-tetradecen-1-yl acetate (**2**) and tetradecan-1-yl acetate (**3**), the active components of the sex pheromone of the Asian Corn Borer moth were synthesized by two different methods, one from acetylene and 11-bromo-1-undecanol THP ether by acetylenic route, the other from 12-acetoxy-1-dodecanal and ethyldienetriphenylphosphonium ylide by Wittig route.

Introduction

Recently O.Saito *et al.*¹ isolated (Z)-12-tetradecen-1-yl acetate (**1**), (E)-12-tetradecen-1-yl acetate (**2**) and tetradecan-1-yl acetate (**3**) (Figure 1) as active components of the female sex pheromone of the Asian Corn Borer moth, *Ostrina furnacalis* Guenee, which is a major economic pest of the corn in Asia.

In 1980, J.A.Klun *et al.*² also isolated this pheromone and synthesized the two components, (Z)-12-tetradecen-1-yl acetate (**1**) and (E)-12-tetradecen-1-yl acetate (**2**).

In spite of the natural rate of 102:117:81 of (Z)-12-tetradecen-1-yl acetate (**1**), (E)-12-tetradecen-1-yl acetate (**2**) and tetradecan-1-yl acetate (**3**), the activity was enhanced by mixing the two compounds in the ratio of 1:1 of (Z)-12-tetradecen-1-yl acetate (**1**) and (E)-12-tetradecen-1-yl acetate (**2**). Including tetradecan-1-yl acetate (**3**) in this natural ratio in pheromone traps resulted in a decrease in trap catches⁴.

Generally pheromonal activity is sensitive to insect species, place and climate. Institute of Agricultural Sciences in Suwon, Korea needed a fair amount of the pheromone of the Asian Corn Borer moth to conduct field test experiments. Therefore we undertook to develop convenient and practical methods for the synthesis of the pheromone of the Asian Corn Borer moth.

Here we wish to report two synthetic routes to the pheromone of the Asian Corn Borer moth and the results of the

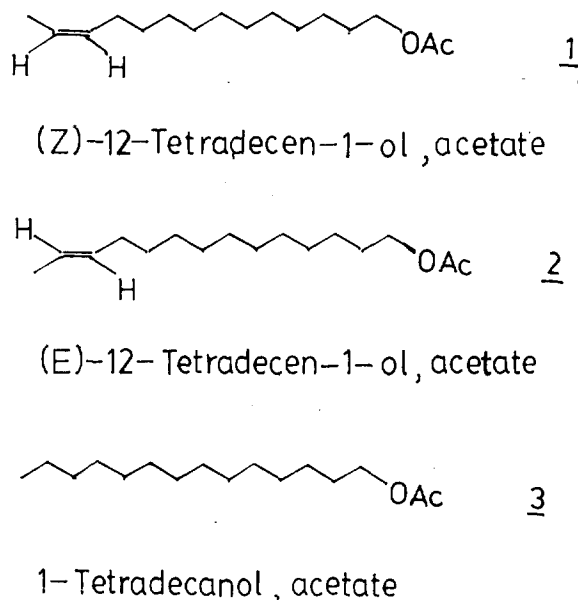


Figure 1

biological activity test of the synthetic pheromones as attractants for males of the Asian Corn Borer moth.

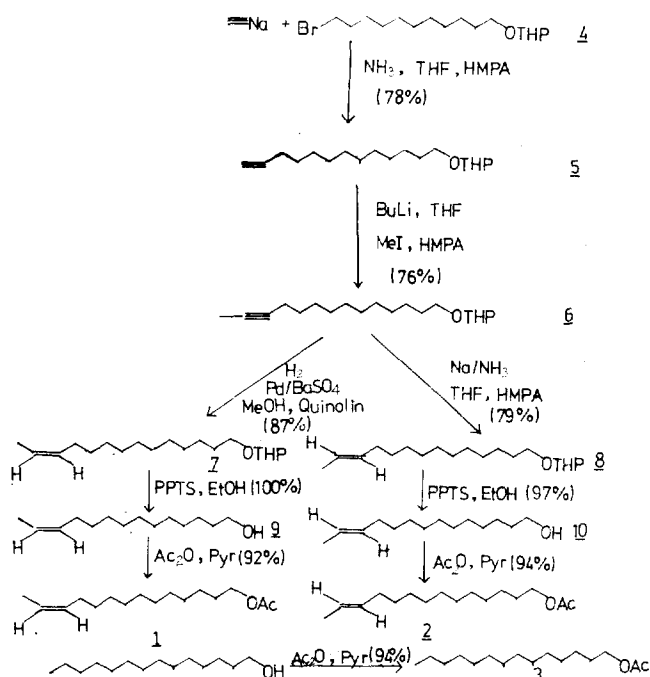
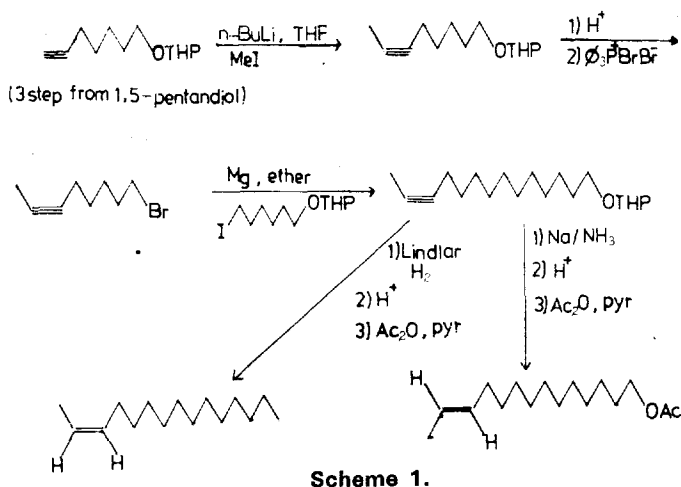
Results and Discussion

Synthesis by J.A.Klun²; The pheromones **1** and **2**, the components of the pheromone the Asian Corn Borer moth, were synthesized by J.A.Klun *et al.* by Grignard coupling reaction of 6-octynylmagnesium bromide and 6-iodo-1-hexanol THP ether, whose preparations are summarized in Scheme 1.

We developed the following two cost-effective synthetic

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methods for the synthesis of (*Z*)-12-tetradecen-1-yl acetate (**1**) and (*E*)-12-tetradecen-1-yl acetate (**2**).

Method 1 (Acetylenic Route). 11-Bromo-1-undecanol THP ether (**4**) was easily prepared from 11-bromo-1-undecanol and 2,3-dihydroxyran in the presence of catalytic amount of pyridinium *p*-toluenesulfonate (PPTS)⁵. In liquid ammonia, with THF and HMPA as cosolvents, sodium acetylide could be alkylated with 11-bromo-1-undecanol THP ether (**4**) to give 12-tridecyn-1-ol THP ether (**5**). 12-Tridecyn-1-ol THP ether (**5**) was then reacted with *n*-butyl lithium in THF to give the lithium acetylide, which was treated with methyl iodide with HMPA as a cosolvent to afford 12-tetradecyn-1-ol THP ether (**6**). 12-Tetradecyn-1-ol THP ether was stereoselectively reduced over Lindlar catalyst (Pd/BaSO₄)⁷ to give (*Z*)-12-tetradecen-1-ol THP ether (**7**). On the other hand, in order to obtain (*E*)-12-tetradecen-1-ol THP ether, 12-tetradecyn-1-ol THP ether (**6**) was reduced with sodium in THF-liquid ammonia⁸. (*Z*)- and (*E*)-12-Tetradecen-1-ol THP ether thus obtained were deprotected by refluxing in

the presence of PPTS and ethanol⁵. (*Z*)- and (*E*)-12-Tetradecen-1-ol were acetylated with acetic anhydride and pyridine to afford the final products, (*Z*)-12-tetradecen-1-yl acetate (**1**) and (*E*)-12-tetradecen-1-yl acetate (**2**), respectively. Tetradecan-1-yl acetate (**3**) was easily synthesized from 1-tetradecanol and acetic anhydride in the presence of pyridine.

Method 2 (Wittig route). A convergent synthesis of (*Z*)-12-tetradecen-1-yl acetate (**1**) and (*E*)-12-tetradecen-1-yl acetate (**2**) was accomplished by Wittig reaction. It has been well established that Wittig reaction when carried out between aldehyde and aliphatic nonstabilized triphenyl-phosphonium ylide in salt-free, nonpolar solvent or in polar aprotic solvents such as DMF, DMSO, or HMPA gives (*Z*)-alkenes stereoselectively⁹. Also it has been well known that Schlosser's modification¹⁰ of Wittig reaction gives (*E*)-alkenes stereoselectively.

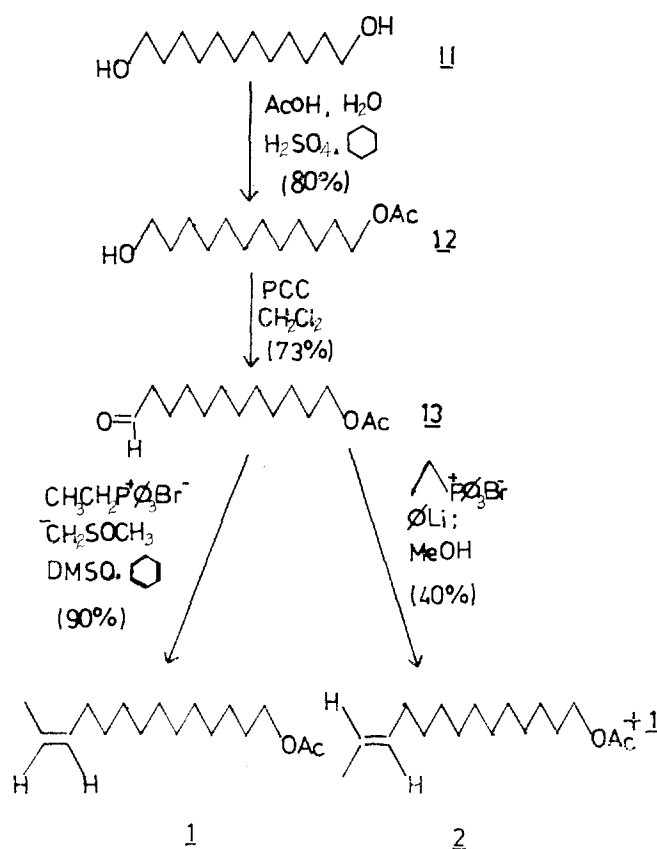
Both (*Z*)-12-tetradecen-1-yl acetate (**1**) and (*E*)-12-tetradecen-1-yl acetate (**2**) were synthesized in three steps from 1,12-dodecandiol, which is cheap and readily available.

Monoacetylation of 1,12-dodecandiol (**11**) in acetic acid and sulfuric acid with continuous extraction method¹¹ afforded 1,12-dodecandiol monoacetate (**12**) in 80 % yield. PCC oxidation gave 12-acetoxy-1-dodecanal (**13**). Wittig reaction of the resulting 12-acetoxy-1-dodecanal and ethyl-triphenylphosphonium bromide in the presence of dimethyl sodium and DMSO and benzene afforded (*Z*)-12-tetradecen-1-yl acetate (**1**) in 90 % yield. The ratio of *cis* (*Z*-) and *trans* (*E*-) was 96:4 by gas chromatography with Carbowax 20M. Theoretically, by using Schlosser's modification of Wittig reaction, (*E*)-12-tetradecen-1-yl acetate (**2**) was expected to form. Unexpectedly by our experiment (*E*)- and (*Z*)-12-tetradecen-1-yl acetate were obtained in the ratio of *ca.* 50:50 by gas chromatography, but this ratio of (*E*)- and (*Z*)-12-tetradecen-1-yl acetate is in the range of enhanced pheromonal activity of the Asian Corn Borer moth. Olefination was carried out by adding 12-acetoxy-1-dodecanal (**13**) to ethylidene-triphenylphosphonium ylide generated in situ from ethyltriphenylphosphonium bromide and phenyl lithium in THF and then treating with methanol.

These two synthetic methods described above were considered to be economic, which are adaptable to large scale preparation.

Biological Activity. Preliminary test was conducted at a corn field located in Suwon to establish that the synthetic pheromone was attractive to males of the Asian Corn Borer moth. In this experiment, a mixture of 102 μg of (*Z*)-12-tetradecen-1-yl acetate, 117 μg of (*E*)-12-tetradecen-1-yl acetate and 81 μg of tetradecan-1-yl acetate was used as an attractant for the Asian Corn Borer moth. Three pheromone vials and one light trap were tested on 30 consecutive nights from the 21th, May, 1983 to the 20th, June, 1983.

Comparison of the efficacy of a pheromone baited trap versus a light trap indicated that the pheromone baited trap could serve as a more convenient monitoring tool: the pheromone trap captured 11-24 males/30 nights while the light trap captured 8 males/30 nights.



Experimental

Infrared spectra were recorded with Perkin-Elmer 735B and Shimadzu IR-440 grating infrared spectrometers. Proton NMR was taken on a Varian 60-MHz spectrometer and Bruker WP80 SY Spectrometer, using the deuterium substituted chloroform for solvent and tetramethylsilane as an internal reference.

Mass spectra were determined with a Jeol JMS-DX 300 mass spectrometer and G.C analyses were performed on a Varian 3700 gas chromatography. All solvents and liquid compounds were distilled before use.

11-Bromo-1-undecanol THP ether (4); A solution of 11-bromo-1-undecanol (2.52g) and 2,3-dihydropyran (1.26g) in dry methylene chloride (25ml) containing PPTS (250mg) was stirred for 5 hrs at room temperature. After methylene chloride was evaporated, the residue was extracted with ether and washed with saturated brine to remove the catalyst. The organic solution was dried over $MgSO_4$ and concentrated in vacuo to give 11-bromo-1-undecanol THP ether (4) (3.29g, 98%). IR: -OH peak (disappeared), NMR: δ 1.30-2.65 (24H), 3.30-4.10 (6H), 4.50 (1H)

12-Tridecyn-1-ol THP ether (5); A three neck flask was fitted with a Dewar condenser which was attached to a gas bubbler with a soda lime drying tube. After nitrogen gas was carried, ammonia gas (dried with KOH) was liquified to 50ml volume. Metallic sodium (0.37g) was dissolved with inletting acetylene gas for about 1 h at $-40^\circ C - -60^\circ C$. To

TABLE 1: The Attractant Effect of the Males of the Asian Corn Borer for the Synthetic Pheromone

Date	The number of male which were caught in 3 Trap			Light Trap
	A	B	C	
5.21-5.25	1	1	0	4
5.26-5.31	16	1	1	3
6.1-6.5	3	2	6	0
6.6-6.10	2	1	1	1
6.11-6.15	1	2	1	1
6.16-6.20	1	4	2	0
Total	24	11	11	8

this solution was added dropwise 11-bromo-1-undecanol THP ether (4) (3.35g) in THF (5ml) and HMPA (5ml) and stirred for 2 hrs at $-20^\circ C$ and for 1 h at room temperature. Ammonia was evaporated, the organic layer was washed with ammonia-water (10ml: 30ml), 6N-HCl, and saturated sodium bicarbonate solution and dried over anhydrous K_2CO_3 . Concentration in vacuo and distillation on Kugelrohr ($148^\circ C$, 4 mmHg) gave 12-tridecyn-1-ol THP ether (5) (2.18 g, 78 %). IR: 3300, 2940, 2250, 1450 cm^{-1} , NMR: δ 1.30-2.15 (26H), 2.25 (1H), 3.27-4.10 (4H), 4.60 (1H).

12-Tetradecyn-1-ol THP ether (6); To a stirred and ice cooled solution of 12-tridecyn-1-ol THP ether (5) (2.80g) in dry THF (5ml) was added dropwise a solution of n-butyllithium in 1.6M n-hexane (10.0ml). The solution was stirred for 15 minutes at room temperature. Then a solution of methyl iodide (1.70 g) in dry HMPA (9ml) was added dropwise to the stirred an ice-cooled mixture. The mixture was stirred for 2 hrs at $0^\circ C - 5^\circ C$ and poured into ice-water. The organic layer was extracted with ether and washed with water and brine. The ether layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was distilled on Kugelrohr ($150^\circ C$, 4 mmHg) to give 12-tetradecyn-1-ol THP ether (6) (2.25 g, 76 %). IR: 3300 (disappeared), 2950, 2250, 1450 cm^{-1} , NMR: δ 1.20-2.00 (29H), 3.10-4.10 (4H) 4.60 (1H).

(Z)-12-Tetradecen-1-ol THP ether (7); To a solution of 12-tetradecyn-1-ol THP ether (6) (0.29g) in methanol (10ml) were added 5 % -palladium on barium sulfate (35 mg) and quinoline (2 drops). The mixture was stirred under hydrogen atmosphere for 12 hrs and filtered to remove the catalyst. Methanol was evaporated in vacuo. The residue was extracted with ether and washed 6N-HCl, water and brine. The organic solution was dried over $MgSO_4$ and concentrated in vacuo to give (Z)-12-tetradecen-1-ol THP ether (7) (0.26g, 87 %). IR: 2950, 2250 (disappeared), 1450, 730 cm^{-1} , NMR: δ 1.20-1.95 (29H), 3.15-4.10 (4H), 4.50 (1H), 5.10-5.45 (2H).

(E)-12-Tetradecen-1-ol THP ether (8); A small piece of sodium (0.92g) was added portionwise to a stirred solution of 12-tetradecyn-1-ol THP ether (6) (1.47g) in dry THF (10ml) and liquid ammonia (30ml) at $-40 - 35^\circ C$. After the sodium was completely dissolved, the cooling bath was removed and the reaction mixture was subjected to reflux (dry ice condenser) for 6 hrs and then quenched with saturated ammonium chloride solution (25ml). The ammonia gas was

allowed to evaporated. The residue was extracted with ether and washed with 1N-HCl, saturated sodium bicarbonate solution and brine. This organic solution was dried over $MgSO_4$ and concentrated in vacuo, distilled on Kugelrohr under reduced pressure ($142^\circ C/3mmHg$) to give (E)-12-tetradecen-1-ol THP ether (8) (1.17g, 79 %). IR: 2945, 2250 (disappeared), 1450, 960 cm^{-1} , NMR: δ 1.10-2.00 (29H) 3.10-4.05 (4H), 4.55(1H), 5.10-5.60(2H).

(Z)-12-Tetradecen-1-ol (9); A solution of (Z)-12-tetradecen-1-ol THP ether (7) (0.30g) and PPTS (25mg) in ethanol (10ml) was stirred at $55^\circ C$ for 4 hrs. The solvent was evaporated in vacuo and the residue was evaporated with ether and washed with 6N-HCl, water and brine and dried over $MgSO_4$. Concentration in vacuo gave (Z)-12-tetradecen-1-ol (9) (0.21g, 100 %). IR: 3350, 2910, 1450, 1050, 730 cm^{-1} , NMR: δ 1.10-1.80 (23H), 1.85 (1H), 3.50-3.85 (2H), 5.10-5.70 (2H).

(E)-12-Tetradecen-1-ol (10); A solution of (E)-12-tetradecen-1-ol THP ether (8) (0.30g) and PPTS (25mg) in ethanol (10ml) was stirred at $55^\circ C$ for 4 hrs. The solvent was evaporated in vacuo and the residue was extracted with ether and washed with 6N-HCl, water and brine and dried over $MgSO_4$. Concentration in vacuo gave (E)-12-tetradecen-1-ol (10) (0.21g, 97 %). IR: 3300, 2920, 1450, 1050, 960 cm^{-1} , NMR: δ 1.10-2.00 (23H), 2.30 (1H), 3.45-3.80 (2H), 5.10-5.75 (2H).

(Z)-12-Tetradecen-1-yl acetate (1); To a solution of (Z)-12-tetradecen-1-ol (9) (0.21g) in dry pyridin (2ml) was added acetic anhydride (0.13g). The mixture was stirred overnight at room temperature, poured into ice-water and extracted with ether. The ether solution was washed with 5% -HCl, saturated sodium bicarbonate solution and brine and dried over $MgSO_4$. Concentration in vacuo and distillation on Kugelrohr ($138^\circ C/3mmHg$) gave (Z)-12-tetradecen-1-yl acetate (1) (0.21g, 84 %). IR: 3350 (disappeared), 2950, 1735, 1450, 1215, 730 cm^{-1} , NMR: δ 1.10-1.75 (23H), 2.00 (3H), 3.90-4.35 (2H), 5.15-5.50 (2H), MS: m/e 194 ($M^+ - CH_3CO_2H$).

(E)-12-Tetradecen-1-yl acetate (2); To a solution of (E)-12-tetradecen-1-ol (10) (0.21g) in dry pyridine (2ml) was added acetic anhydride (0.13g). The mixture was stirred overnight at room temperature and extracted with ether. The ether solution was washed with 5% -HCl, saturated sodium bicarbonate solution and brine. The organic solution was dried over $MgSO_4$ and concentrated in vacuo, followed by distillation on Kugelrohr under reduced pressure ($136^\circ C/3mmHg$) to give (E)-12-tetradecen-1-yl acetate (2) (0.23g, 92 %). IR: 3350 (-OH peak disappeared), 2943, 1740, 1450, 960 cm^{-1} , NMR; δ 1.15-1.75 (23H), 2.10 (3H), 3.95-4.3 (2H), 5.10-5.55 (2H), MS: m/e 194 ($M^+ - CH_3CO_2H$).

Tetradecan-1-yl acetate (3); Acetic anhydride (0.12ml) was added to a solution of 1-tetradecanol (0.21 g) in dry pyridine (2ml). The mixture was stirred overnight at room temperature and extracted with ether.

The ether solution was washed with 5% -HCl, saturated sodium bicarbonate solution and brine. The organic solution was dried over $MgSO_4$ and concentrated in vacuo, distilled on Kugelrohr under reduced pressure ($125^\circ C/3mmHg$) to

give tetradecan-1-yl acetate (3) (0.24g, 94 %). IR: 3350 (-OH peak disappeared), 2920, 1735, 1450, 1050 cm^{-1} , MS: m/e 196 ($M^+ - CH_3CO_2H$).

1,12-Dodecanediol monoacetate (12); A solution of 1,12-dodecane-diol (11) (0.50g) in 10ml of glacial acetic acid was mixed with H_2O (13ml) containing conc. H_2SO_4 (0.023ml). This mixture was extracted continuously for 2 days using refluxing cyclohexane with continuous extraction apparatus. The cyclohexane layer was cooled, crystalline 1,12-dodecanediol was recovered by simple filtration. The cyclohexane layer was evaporated under reduced pressure and afforded the crude product (0.52g). The crude product was separated by flash column chromatography with ether: petroleum ether (1:1) as solvent, followed by distillation on Kugelrohr under reduced pressure ($130^\circ/4mmHg$) to yield the diolmonoacetate (12, 0.45g, 80 % yield). TLC: Rf 0.34 (50 % ether: petroleum), NMR: δ 4.0 (2H, t), 3.5 (2H, t), 2.2 (1H, s), 1.9 (3H, s), 1.8-1.1 (18H, m).

12-acetoxy-1-dodecanal (13); To a mixture of PCC (0.36g) in dry dichloromethane (5ml) was added 1,12-dodecanediol monoacetate (12) (0.26g), and the mixture was stirred for 2 hrs at room temperature. The reaction mixture was poured into dry ether (30ml) with stirring, and filtered through florisil bed. Concentration and distillation under reduced pressure ($142^\circ C/4mmHg$) to give the pure aldehyde (13, 0.20g, 73 % yield). IR: 2900, 2700, 1740, 1460, 1370, 1240, 1040 cm^{-1} , NMR: δ 9.78 (1H, t), 4.0 (3H, t), 2.4 (2H, t), 2 (4H, s), 1.8-1.1 (16H, m).

(Z)-12-Tetradecen-1-yl acetate (1); To a solution of dimethyl sodium (NaH (0.042g) and dimethyl sulfoxide (0.17ml)) under nitrogen atmosphere was added ethyl triphenylphosphonium bromide (0.89g) in DMSO (5ml). To the reaction mixture was added 12-acetoxy-1-dodecanal (13, 0.10g) in DMSO (1ml) and diluted with dry benzene (6.6ml). The reaction mixture was stirred at room temperature for 3 hrs and added H_2O (15ml) and extracted with ether: n-hexane (1:1). The ether-hexane layer was separated and washed with H_2O and dried over $MgSO_4$. Concentration and distillation on Kugelrohr under reduced pressure ($133^\circ C/4mmHg$) afforded the (Z)-alkene (1, 0.09g, 90 % yield). The ratio of *cis* (Z-) and *trans* (E-) was 96:4 by gas chromatography with Carbowax 20M on Varian 3700. IR: 3020, 2900, 1740, 1460, 1370, 1235, 1040, 960, 700 cm^{-1} , NMR: δ 5.4 (2H, t, J=6Hz), 4 (3H, t) 2 (4H, s), 1.8 - 1.1 (21H, m), MS: m/e 194 ($M^+ - CH_3CO_2H$).

(E)-12-Tetradecen-1-yl acetate and (Z)-12-Tetradecen-1-yl acetate; To a solution of ethyltriphenylphosphonium bromide (0.36g) in THF (1ml) and ether (0.6ml) was added 2.7M ethereal phenyl lithium (0.28ml) at room temperature under nitrogen atmosphere. After The temperature decrease to $-70^\circ C$, 12-acetoxy-1-dodecanal (0.20g) in ether (0.2ml) was added to this solution and stirred for 10 mins and then warmed to $-30^\circ C$. To this reaction mixture, methanol (0.21ml) was added and then warmed to room temperature for 2 hrs. The mixture was poured into H_2O (10ml) and extracted with ether and wash with water. After evaporation, pentane (5ml) was added and filtered through the Silica gel bed. The filtrate

was dried over MgSO_4 and distillation under reduced pressure ($135^\circ\text{C}/4\text{mmHg}$) afforded the (E)-alkene (**2**) and (Z)-alkene (**1**) (0.08g, 40% yield). The ratio of *trans* (E-) and *cis* (Z-) was 50:50 by gas chromatography with Carbowax 20M on Varian 3700. IR: 3020, 2900, 1740, 1600, 1450, 1360, 1240, 1040, 960, 925, 905, 700 cm^{-1} , NMR: δ 5.4 (2H, t, J=8Hz), 4 (3H, t), 2 (4H, s), 1.8-1.1 (21H, m), MS: m/e 194 ($\text{M}^+ - \text{CH}_3\text{CO}_2\text{H}$).

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Solvation in Mixed Solvents (IV). Solvolysis of Adamantyl Derivatives in Methanol-Acetonitrile Mixtures

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Solvolysis of 1-adamantyl chloride, -bromide and -tosylate have been studied in methanol-acetonitrile mixtures. Rate maxima were found for 1-adamantyl bromide and tosylate at 80-90 % methanol mixtures. The rate maximum observed was interpreted as a result of cooperative enhancement of cation and anion solvation. 1-Adamantyl tosylate had small cation solvation but had extensive anion solvation. It was concluded that the *Y* scale based on adamantyl tosylate is superior to others since it varies in a wide range especially for weakly ionizing medium.

Solvolysis of *tert*-butyl halides have received considerable attention in the study of solvent effects on rates of chemical reactions.¹⁻⁷ Grunwald and Winstein¹⁻³ introduced equation (1) for correlating solvent dependence of rates of organic reactions.

$$\log k = \log k_0 + mY \quad (1)$$

where k and k_0 are the rates of a reaction in a solvent of ionizing power Y and in the reference solvent, 80% ethanol-water mixture, respectively. The m represents susceptibility of the reaction to solvent ionizing power Y , and is unity for *tert*-butyl chloride solvolysis at 25°C . It was assumed that the rate determining step of the solvolysis of *tert*-butyl chloride

in hydroxylic solvent is the heterolysis of C-Cl bond in the $\text{S}_{\text{N}}1$ process and is not sensitive to solvent nucleophilicity¹. However Bentley *et al*⁸, argued that comparison of solvolysis rates for 1- or 2-adamantyl compounds with those for *tert*-butyl halides shows involvement of solvent nucleophilicity in *tert*-butyl halides solvolysis. Swain *et al*⁹, have also reported that solvolysis of *tert*-butyl halides are influenced by the solvent nucleophilicity.

In this respect adamantyl derivatives are to be preferred to *tert*-butyl halides in the determination of solvent ionizing power Y ^{8,10-17}. Adamantyl compounds have rigid, caged structure and rear-side nucleophilic attack is impossible sterically so that a limiting $\text{S}_{\text{N}}1$ mechanism is assured for the