A General Approach to the Synthesis of Mono-olefinic Insect Sex Pheromones of *Z*- or *E*-Configuration.

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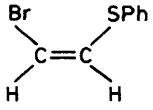
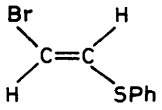
A series of insect sex pheromones and structurally related olefins have been synthesized with high stereoisomeric purity by two sequential cross-coupling reactions. Starting with (*Z*)- or (*E*)-1-bromo-2-phenylthioethene, (**1**) and (**2**), and Grignard reagents in the presence of nickel or palladium catalysts, two types of compounds have been prepared: (i) 1,2-dialkylethenes and (ii) alkenyl acetates. In the synthesis of the *Z*-isomers, the first step involves a cross-coupling reaction of compound (**1**) with the appropriate Grignard reagent in the presence of a catalytic amount of $[PdCl_2(PPh_3)_2]$. The second cross-coupling reaction is performed on the intermediate (*Z*)-phenylthioalkenes using a different Grignard reagent in the presence of $[NiCl_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) as a catalyst. In the synthesis of *E*-isomers both steps are cross-coupling reactions of Grignard reagents in the presence of $[NiCl_2(dppe)]$ as a catalyst, the first step involving compound (**2**) and the second step involving the intermediate (*E*)-phenylthioalkenes obtained. The Grignard reagents used in the synthesis of the alkenyl acetates derive from protected ω-halohydrins.

In a recent communication [1] we reported a simple stereospecific procedure leading to (*Z*)- or (*E*)-1, 2-disubstituted ethenes. The procedure involves two cross-coupling reactions between Grignard reagents and the readily available [2] (*Z*)- or (*E*)-1-bromo-2-phenylthioethene, (**1**) or (**2**), in the presence of a Ni^{II} or



(**1**)



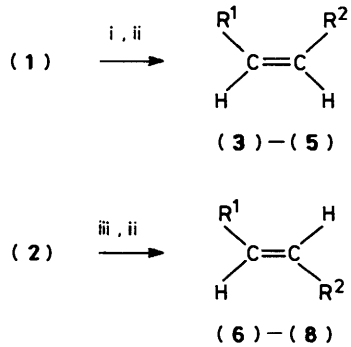
(**2**)

Pd^{II} complex as a catalyst.[3] In the first step, substitution of the bromine occurs at a rate which is sufficiently fast to leave the C–S bond completely unaffected. Using longer reaction times and an excess of Grignard reagent, it was possible to perform the slower reaction leading to the substitution of the phenylthio group. When non-symmetrical olefins were required it was only necessary to use a different Grignard reagent after completion of the first step. The isomeric purity of the final product was higher than 99% in the case of the *E*-isomers and in the range 95—98% for the *Z*-isomers. In the synthesis of *Z*-isomers the use of a Pd catalyst during the first step was found to give better stereochemical results. The overall yields (as determined by g.l.c. analysis) were in the range 50—100%.

Our method presented several interesting features. Therefore, with the aim of exploring the scope and limitations of the procedure, we decided to synthesize a series of mono-olefinic pheromones, simple 1,2-dialkylethenes or alkenyl acetates, which have attracted a great deal of attention from the synthetic point of view.[4–14] We now report the results of our investigation. This will also allow us to give for the first time a full account of our sequential cross-coupling procedure.

Results and Discussion

Synthesis of 1,2-*Dialkylethenes* (**3**)—(**8**).—(*Z*)-Tricos-9-ene (muscalure) (**3**),[4,5] the sex pheromone of the housefly (*Musca domestica*)[15] and (*Z*)-heneicos-9-ene (**4**),[5a] whose effectiveness, when mixed with (**3**), is rather controversial,[16] were prepared according to the procedure reported in Scheme 1. The same



(**3**), (**6**) $R^1 = n\text{-}C_{13}H_{27}$; $R^2 = n\text{-}C_8H_{17}$

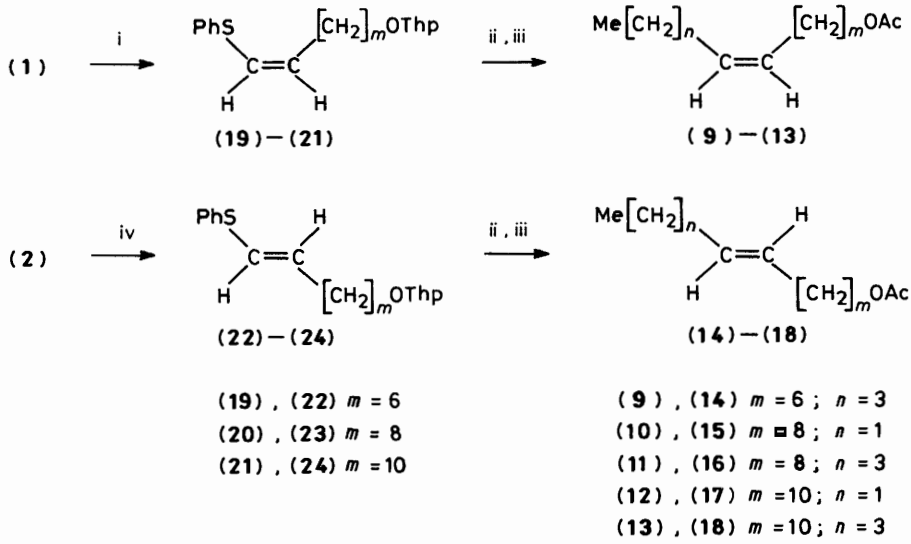
(**4**), (**7**) $R^1 = n\text{-}C_{11}H_{23}$; $R^2 = n\text{-}C_8H_{17}$

(**5**), (**8**) $R^1 = n\text{-}C_{10}H_{21}$; $R^2 = Me_2CH[CH_2]_4$

Scheme 1. *Reagents*: i, R^1MgBr–$[PdCl_2(PPh_3)_2]$; ii, R^2MgBr–$[NiCl_2(dppe)]$; iii, R^1MgBr–$[NiCl_2(dppe)]$

Scheme shows the route to (*Z*)-2-methyl-octadec-7-ene (**5**),[4a,c,6] which upon oxidation gives (*Z*)-7,8-epoxy-2-methyl-octadecane[4a,c,6] (disparlure), the sex pheromone of the gypsy moth (*Porthetria dispar*).[17] The overall isolated yields were in the range 65—75% and the isomeric purities were higher than 98%. The preparation of the corresponding stereoisomers (*E*)-tricos-9-ene (**6**),[5e,7] (*E*)-heneicos-9-ene (**7**), and (*E*)-2-methyl-octadec-7-ene (**8**)[8] can be easily accomplished starting with (*E*)-1-bromo-2-phenylthioethene (**2**) (Scheme 1) with overall isolated yields in the range 85—90% and isomeric purities higher than 99%. In the case of both types of isomers the intermediate alkenyl phenyl sulphides were not isolated and the Grignard reagent for the second cross-coupling reaction was added directly to the reaction mixture. As in previous cases,[1] in order to obtain good stereochemical results a Pd^{II} complex had to be used during the first step of the preparation of the *Z*-isomers.

Synthesis of Alkenyl Acetates (**9**)—(**18**).—The procedure followed for the synthesis of pheromones having a (*Z*)-alkenyl



Scheme 2. *Reagents*: i, $ThpO[CH_2]_mMgX$–$[PdCl_2(PPh_3)_2]$; ii, $Me[CH_2]_nMgBr$–$[NiCl_2(dppe)]$; iii, Ac_2O; iv, $ThpO[CH_2]_mMgX$–$[NiCl_2(dppe)]$

acetate structure is shown in Scheme 2. Grignard reagents obtained from 1-halogeno-ω-tetrahydropyranyloxyalkanes were mixed with compound (**1**), at room temperature and in the presence of $[PdCl_2(PPh_3)_2]$ as a catalyst, to give 1-phenylthio-ω-tetrahydropyranyloxyalk-1-enes (**19**)—(**21**). The second cross-coupling reaction with the appropriate Grignard reagent in the presence of a catalytic amount of $[NiCl_2(dppe)]$ led to the tetrahydropyranyloxy-protected alkenols which were subjected directly to acetylation with acetic anhydride[18] at 80 °C, to give (*Z*)-dodec-7-enyl acetate (**9**),[4,9] (*Z*)-dodec-9-enyl acetate (**10**),[4c,10] (*Z*)-tetradec-9-enyl acetate (**11**),[4a,b,9a,c,d,f,10a] (*Z*)-tetradec-11-enyl acetate (**12**),[4a,b,6a,9a,c,11] and (*Z*)-hexadec-11-enyl acetate (**13**).[4a,b,6a,9a,d,11,12] The overall isolated yields were in the range 52—60% and the isomeric purities were higher than 97%.

Compound (**9**) is the sex pheromone of the cabbage looper (*Trichoplusia ni*)[19] and also of the soybean looper (*Pseudoplusia includens*).[20] Compound (**10**) is the sex pheromone of the female grapeberry moth (*Paralobesia viteana*)[21] and of *Eupoecilia ambiguella*.[22] Compound (**11**) is a component of the pheromones of the smaller tea tortrix (*Adoxophyes fasciata*),[23] the fall armyworm (*Spodoptera frugiperda*),[24] and the black cutworm moth (*Agrotis ypsilon*).[25] Compound (**12**) is a component of the pheromones of several tortricid moths, including *Choristoneura rosaceana*,[26] *Argyrotaenia velutinana*,[27] *A. citrana*,[28] *Archips rosanus*,[29] and *Ostrinia nubilalis*.[30] Compound (**13**) is the sex pheromone component of the cabbage armyworm moth (*Mamestra brassicae*).[31]

As shown in Scheme 2, the synthesis of the corresponding stereoisomers (*E*)-dodec-7-enyl acetate (**14**),[4,9c,13] (*E*)-dodec-9-enyl acetate (**15**),[4c,13d,f] (*E*)-tetradec-9-enyl acetate (**16**),[9c] (*E*)-tetradec-11-enyl acetate (**17**),[6a,9c,11a,13d–f] and (*E*)-hexadec-11-enyl acetate (**18**)[6a,11a,13d,14] was accomplished by treating compound (**2**) with Grignard reagents in the presence of $[NiCl_2(dppe)]$ as a catalyst. At variance with the synthesis of the *Z*-isomers, the same catalyst was used in the second cross-coupling reaction, which involved the appropriate Grignard reagents and the intermediate alkenyl phenyl sulphides (**22**)—(**24**). The overall isolated yields were in the range 62—70% and the isomeric purities higher than 99.5%

Compound (**14**) is the pheromone of the false codling moth (*Cryptophlebia leucotreta*).[32] Compound (**15**) is the pheromone of the European pine shoot moth (*Rhyacionia buoliana*),[33] whereas compound (**16**) is a synthetic attractant of *Polia grandis*[34] and *Loxostege neobliteralis*.[34] Compound (**17**) is a pheromone component of *Archips mortuanus*[35] and a synthetic attractant of other tortricid moths.[9c] Compound (**18**) is the major component of the sex pheromone of *Bracmia macroscopa*.[14]

Conclusions.—A variety of procedures[4–14] have been previously adopted for the synthesis of the products of the present investigation. Most frequently, classical methods have been used, such as the stereoselective reduction of an acetylenic compound[4,6a,8b,9a,c,f] or the Wittig reaction.[4,5a,6c,9e,11b,13f] Taking into account (i) the mild reaction conditions (all of the cross-coupling reactions being performed at room temperature), (ii) the simplicity of the operations involved, (iii) the relatively high overall yields, and (iv) the high stereospecificity, from a comparison with previous work, our method appears to rank among the most useful procedures presently available for the synthesis of 1,2-disubstituted ethenes.

Experimental

^1H N.m.r. spectra were recorded on a Varian EM 390 spectrometer (90 MHz) in tetrachloromethane. Chemical shifts are expressed as δ values, using tetramethylsilane as an internal standard. The i.r. spectra refer to films and were recorded on a Perkin-Elmer 681 instrument. Mass spectra were taken on a Kratos M60 (70 ev) spectrometer. Elemental analyses were performed on a Hewlett-Packard 185 analyser. The g.l.c. analyses were performed on a Hewlett-Packard 5830A chromatograph and on a Dani 3800 capillary columns dedicated instrument using fused silica capillary columns (30 m × 0.25 mm i.d., carrier He, 0.6 bar) containing SE 30 or Carbowax 20M as stationary phases for 1,2-dialkylethenes (**3**)—(**8**) and alkenyl acetates (**9**)—(**18**) respectively. Boiling points are uncorrected.

Materials.—Diethyl ether and THF (RS Carlo Erba) were purified by two distillations from Na wire under nitrogen. (*Z*)- and (*E*)-1-Bromo-2-phenylthioethene, (**1**) and (**2**), were obtained according to the procedure of Montanari and his co-workers[2] by addition of PhSH to propiolic acid in ethanol and subsequent one-pot bromine addition and decarboxylative dehalogenation to give (**1**) and (**2**) in *ca.* 4:1 ratio. The *E*-isomer was removed from the mixture by careful distillation on a Fischer column HMS 500 at 49.5 °C/0.04 Torr, and the recovered *Z*-isomer was purified by straightforward distillation (b.p. 59—60 °C/0.04 Torr). Bromoethane, 1-bromobutane, and 1-bromo-octane were commercial products. 1-Bromodecane,

1-bromoundecane, 1-bromotridecane, and 1-bromo-5-methylhexane were prepared from the corresponding alcohols by treatment with HBr (48%) and concentrated H_2SO_4; the alcohols were commercial products, with the exception of 5-methylhexan-1-ol[8b] which was prepared from 5-methylhex-1-ene (Fluka) by hydroboration–oxidation.[36] 6-Chlorohexan-1-ol was commercially available whereas 8-bromo-octan-1-ol and 10-bromodecan-1-ol were prepared from the corresponding alkanediols by treatment with HBr (48%) at 100 °C under conditions of continuous extraction with refluxing heptane to give, after column chromatography, the corresponding ω-halohydrins.[37] The protection of the alcoholic function was obtained by treating the halohydrins in hexane with a two-fold excess of 3,4-dihydro-2*H*-pyran in the presence of a catalytic amount of dried Amberlyst H-15[38] to give 1-chloro-6-tetrahydropyranyloxyhexane,[39] 1-bromo-8-tetrahydropyranyloxyoctane,[40] and 1-bromo-10-tetrahydropyranyloxydecane.[10a] $[NiCl_2(dppe)]$ and $[PdCl_2(PPh_3)_2]$ were commercial products (Alfa).

(Z)-*Tricos-9-ene* (**3**), (Z)-*Heneicos-9-ene* (**4**), *and* (Z)-2-*Methyloctadec-7-ene* (**5**).—*General procedure.* A 1.0M ether solution of R^1MgBr (5.5 mmol) was slowly added, under nitrogen, to a stirred suspension of $[PdCl_2(PPh_3)_2]$ (0.15 mmol) and (*Z*)-1-bromo-2-phenylthioethene (**1**) (5.0 mmol) in anhydrous ether (50 ml) at room temperature. After completion of the first cross-coupling reaction (1 h, g.l.c. analysis), $[NiCl_2(dppe)]$ (0.3 mmol) was added to the mixture and a 1.0M ether solution of R^2MgBr (10 mmol) was slowly added dropwise. After being stirred for 12 h at room temperature, the mixture was poured into water and extracted with ether. The combined extracts were washed with aqueous NaOH (10%) and with water, dried (Na_2SO_4), and concentrated. By-products were removed by dissolving the residue in acetone, cooling the solution to precipitate a small amount of solid material, evaporating the solvent after filtration, and distilling to give the corresponding alkenes (**3**)—(**5**). (*Z*)-Tricos-9-ene (**3**) (R^1 = n-$C_{13}H_{27}$, R^2 = n-C_8H_{17}) (75% yield, 98.3% stereoisomeric purity) had b.p. 148—150 °C/0.04 Torr (lit.,[5c] 140—142 °C/0.01 Torr); the spectral data were in good agreement with those of an authentic commercial sample. (*Z*)-Heneicos-9-ene (**4**) (R^1 = n-$C_{11}H_{23}$, R^2 = n-C_8H_{17}) (73% yield, 98.1% stereoisomeric purity) had b.p. 118—120 °C/0.04 Torr; the spectral data were in good agreement with those of an authentic commercial sample. (*Z*)-2-Methyloctadec-7-ene (**5**) [R^1 = n-$C_{10}H_{21}$, R^2 = $Me_2CH(CH_2)_4$] (65% yield, 98.3% stereoisomeric purity) had b.p. 98—100 °C/0.08 Torr (lit.,[6b] 100—102 °C/0.05 Torr); the spectral data were as reported.[6b,e,f]

(E)-*Tricos-9-ene* (**6**), (E)-*Heneicos-9-ene* (**7**), *and* (E)-2-*Methyloctadec-7-ene* (**8**).—The title compounds were prepared as in the case of the corresponding *Z*-isomers using (*E*)-1-bromo-2-phenylthioethene (**2**) and $[NiCl_2(dppe)]$ (0.15 mmol) as a catalyst. The second step was performed by adding the Grignard reagent to the mixture containing the catalyst and the products of the first cross-coupling reaction. The g.l.c. analysis showed that the stereochemical purity of the alkenes (**6**)—(**8**) was higher than 99%. (*E*)-Tricos-9-ene (**6**) (R^1 = n-$C_{13}H_{27}$, R^2 = n-C_8H_{17}), (90% yield) had b.p. 138—139 °C/0.04 Torr (lit.,[7b] 164—165 °C/0.35 Torr); $\nu_{max.}$ 3 005, 1 455, 1 373, and 960 cm^{-1}; δ_H 5.30 (m, 2 H), 1.95 (m, 4 H), 1.28 (br s, 34 H), and 0.90 (m, 6 H); *m/z* 322 (M^+, 1%), 125 (7), 111 (17), 97 (43), 83 (65), 69 (76), 57 (100), and 55 (78). (E)-*Heneicos-9-ene* (**7**) (R^1 = n-$C_{11}H_{23}$, R^2 = n-C_8H_{17}) (85% yield) had b.p. 124—126 °C/0.04 Torr; $\nu_{max.}$ 3 005, 1 455, 1 378, and 962 cm^{-1}; δ_H 5.28 (m, 2 H), 1.95 (m, 4H), 1.28 (br s, 30 H), and 0.90 (m, 6 H); *m/z* 294 (M^+, 12%), 125 (22), 111 (48), 97 (92), 83 (100), 69 (74), 57 (66), and 55 (61) (Found: C, 85.5; H, 14.2. $C_{21}H_{42}$ requires C, 85.62; H, 14.37%). (*E*)-2-Methyloctadec-7-ene (**8**) [R^1 = n-$C_{10}H_{21}$, R^2 = $(Me)_2CH(CH_2)_4$] (88% yield) had b.p. 94—96 °C/0.08 Torr (lit.,[8b] 123—124 °C/0.4 Torr); the spectral data were as reported.[8b]

(Z)-2-(8-*Phenylthio-oct-7-enyloxy*)*tetrahydro*-2H-*pyran* (**19**), (Z)-2-(10-*Phenylthiodec-9-enyloxy*)*tetrahydro*-2H-*pyran* (**20**), *and* (Z)-2-(12-*Phenylthiododec-11-enyloxy*)*tetrahydro*-2H-*pyran* (**21**).—*General procedure.* A 0.5M solution (ether–THF 1:1) of $ThpO[CH_2]_mMgX$* (5.5 mmol), was added slowly, under nitrogen, to a stirred suspension of $[PdCl_2(PPh_3)_2]$ (0.15 mmol) and (*Z*)-1-bromo-2-phenylthioethene (**1**) (5.0 mmol) in ether–THF (1:1; 50 ml) at room temperature. After 1 h, g.l.c. analysis revealed the complete disappearance of the starting material. The mixture was then poured into water and extracted with ether (×3). The organic layers were combined, washed with water, dried (Na_2SO_4), and concentrated. Distillation of the residue gave the corresponding *Z*-compounds (**19**)—(**21**), which were sufficiently pure for the further reactions. The isomeric purity of these products was not evaluated; however, it should be higher than or equal to that of the corresponding (*Z*)-alkenyl acetates (*i.e.* ≥97—98%; see below). (Z)-2-(8-*Phenylthio-oct-7-enyloxy*)*tetrahydro*-2H-*pyran* (**19**) (*m* = 6) (75% yield) had b.p. 158—160 °C/0.04 Torr; $\nu_{max.}$ 1 588, 1 482, 1 443, 1 140, 1 122, 1 080, 1 040, and 765 cm^{-1}; δ_H 7.4—6.9 (m, 5 H), 6.2—5.6 (m, 2 H), 4.48 (br, 1 H), 3.9—3.1 (m, 4 H), 2.4—2.0 (m, 2 H), and 2.0—1.1 (br, 14 H); *m/z* 236 (24), 149 (35), 110 (34), 109 (32), and 85 (100) (Found: C, 71.5; H, 8.9; S, 9.85. $C_{19}H_{28}O_2S$ requires C, 71.20; H, 8.81; S, 10.00%). (Z)-2-(10-*Phenylthiodec-9-enyloxy*)-*tetrahydro*-2H-*pyran* (**20**) (*m* = 8) (76% yield) had b.p. 166—168 °C/0.04 Torr; $\nu_{max.}$ 1 588, 1 482, 1 443, 1 140, 1 122, 1 080, 1 037, and 765 cm^{-1}; δ_H 7.4—7.0 (m, 5 H), 6.2—5.5 (m, 2 H), 4.48 (br, 1 H), 3.9—3.1 (m, 4 H), 2.4—2.0 (m, 2 H), and 2.0—1.1 (br, 18 H); *m/z* 264 (8), 149 (19), 110 (36), 109 (46), and 85 (100) (Found: C, 72.6; H, 9.3; S, 9.1. $C_{21}H_{32}O_2S$ requires C, 72.36; H, 9.25; S, 9.20%). (Z)-2-(12-*Phenylthiododec-11-enyloxy*)*tetrahydro*-2H-*pyran* (**21**) (*m* = 10) (71% yield) had b.p. 172—174 °C/0.04 Torr, $\nu_{max.}$ 1 588, 1 480, 1 440, 1 140, 1 120, 1 080, 1 035, and 765 cm^{-1}; δ_H 7.4—7.0 (m, 5 H), 6.2—5.5 (m, 2 H), 4.50 (br, 1 H), 3.9—3.1 (m, 4 H), 2.4—2.0 (m, 2 H), and 2.0—1.0 (br, 22 H); *m/z* 292 (5), 149 (8), 110 (25), 109 (33), and 85 (100) (Found: C, 73.5; H, 9.8; S, 8.45. $C_{23}H_{36}O_2S$ requires C, 73.35; H, 9.64; S, 8.52%).

(Z)-*Dodec-7-enyl Acetate* (**9**), (Z)-*Dodec-9-enyl Acetate* (**10**), (Z)-*Tetradec-9-enyl Acetate* (**11**), (Z)-*Tetradec-11-enyl Acetate* (**12**), *and* (Z)-*Hexadec-11-enyl Acetate* (**13**).—*General procedure.* A 1.0M ether solution of $Me[CH_2]_nMgBr$ (6.0 mmol) was slowly added, under nitrogen, to a stirred suspension of $[NiCl_2(dppe)]$ (0.18 mmol) and (*Z*)-1-phenylthio-ω-tetrahydropyranyloxyalk-1-enes (**19**)—(**21**) (3.0 mmol) in ether (30 ml) at room temperature. After completion of the reaction (12 h, g.l.c. analysis), the mixture was poured into water and extracted with ether (×3). The collected organic phases were washed with aqueous NaOH (10%) (×2) and with water (×2), dried (Na_2SO_4), and concentrated. The crude products obtained were dissolved in acetic anhydride (20 ml) and heated at 80 °C for 15 h. The cooled solution was poured into water and extracted with ether. The ether extracts were washed with aqueous $NaHCO_3$ (5%) and with water, dried, and concentrated. Distillation gave the corresponding acetates (**9**)—(**13**). The spectral data were identical with those of commercial authentic samples. (*Z*)-Dodec-7-enyl acetate (**9**), obtained in 77% yield from (**19**) and n-C_4H_9MgBr, (97.2% stereoisomeric purity), had b.p. 97—99 °C/0.08 Torr (lit.,[9b] 80—81 °C/0.01 Torr). (*Z*)-Dodec-9-enyl acetate (**10**), obtained in 78% yield from (**20**) and

* The Grignard reagents were prepared following the usual procedure[40] (X = Cl, *m* = 6; X = Br, *m* = 8,10).

C_2H_5MgBr, (97.8% stereoisomeric purity), had b.p. 92—95 °C/0.08 Torr (lit.,[10c] 98 °C/0.1 Torr). (*Z*)-Tetradec-9-enyl acetate (**11**) obtained in 75% yield from (**20**) and n-C_4H_9MgBr (97.2% stereoisomeric purity), had b.p. 108—109 °C/0.08 Torr (lit.[9c] 96—97 °C/0.03 Torr). (*Z*)-Tetradec-11-enyl acetate (**12**), obtained in 73% yield from (**21**) and C_2H_5MgBr, (98.2% stereoisomeric purity), had b.p. 104—106 °C/0.08 Torr (lit.,[11b] 103 °C/0.1 Torr). (*Z*)-Hexadec-11-enyl acetate (**13**), obtained in 73% yield from (**21**) and n-C_4H_9MgBr, (97.2% stereoisomeric purity), had b.p. 121—123 °C/0.08 Torr (lit.,[12] 110 °C/0.05 Torr).

(E)-2-(8-*Phenylthio-oct*-7-*enyloxy*)*tetrahydro*-2H-*pyran* (**22**), (E)-2-(10-*Phenylthiodec*-9-*enyloxy*)*tetrahydro*-2H-*pyran* (**23**), *and* (E)-2-(12-*Phenylthiododec*-11-*enyloxy*)*tetrahydro*-2H-*pyran* (**24**).—These compounds were prepared following the same procedure of the corresponding *Z*-isomers starting with (*E*)-1-bromo-2-phenylthioethene (**2**) and using [$NiCl_2$(dppe)] (0.15 mmol) as a catalyst. After distillation, compounds (**22**)—(**24**) were sufficiently pure for the further reactions. The isomeric purity of these products was not evaluated, but it should be higher than or equal to that of the corresponding (*E*)-alkenyl acetates (*i.e.* ⩾99.5%; see below). (E)-2-(8-*Phenylthio-oct*-7-*enyloxy*)*tetrahydro*-2H-*pyran* (**22**) (*m* = 6) (86% yield) had b.p. 148—152 °C/0.04 Torr; $\nu_{max.}$ 1 588, 1 481, 1 442, 1 140, 1 122, 1 080, 1 040, and 955 cm^{-1}; δ_H 7.4—6.9 (m, 5 H), 6.2—5.5 (m, 2 H), 4.48 (br, 1 H), 3.9—3.1 (m, 4 H), 2.4—2.0 (m, 2 H), and 2.0—1.1 (br, 14 H); *m*/*z* 236 (3), 149 (10), 110 (9), 109 (11), and 85 (100) (Found: C, 71.45; H, 8.85; S, 9.85. $C_{19}H_{28}O_2S$ requires C, 71.20; H, 8.81; S, 10.00%). (E)-2-(10-*Phenylthiodec*-9-*enyloxy*)-*tetrahydro*-2H-*pyran* (**23**) (*m* = 8) (83% yield) had b.p. 179—180 °C/ 0.04 Torr; $\nu_{max.}$ 1 590, 1 482, 1 442, 1 138, 1 120, 1 080, 1 037, and 953 cm^{-1}; δ_H 7.3—6.9 (m, 5 H), 6.2—5.6 (m, 2 H), 4.48 (br, 1 H), 3.9—3.1 (m, 4 H), 2.3—2.0 (m, 2 H), and 2.0—1.1 (br, 18 H); *m*/*z* 264 (5), 149 (13), 110 (17), 109 (11), and 85 (100) (Found: C, 72.7; H, 9.4; S, 9.1. $C_{21}H_{32}O_2S$ requires C, 72.36; H, 9.25; S, 9.20%). (E)-2-(12-*Phenylthiododec*-11-*enyloxy*)*tetrahydro*-2H-*pyran* (**24**) (*m* = 10) (85% yield) had b.p. 188—190 °C/0.04 Torr; $\nu_{max.}$ 1 587, 1 482, 1 441, 1 140, 1 122, 1 080, 1 040, and 952 cm^{-1}; δ_H 7.3—7.0 (m, 5 H), 6.2—5.6 (m, 2 H), 4.48 (br, 1 H), 3.9—3.1 (m, 4 H), 2.3—2.0 (m, 2 H), and 2.0—1.1 (br, 22 H); *m*/*z* 292 (2), 149 (7), 110 (19), 109 (31), and 85 (100) (Found: C, 73.5; H, 9.75; S, 8.45. $C_{23}H_{36}O_2S$ requires C, 73.35; H, 9.64; S, 8.52%).

(E)-*Dodec*-7-*enyl Acetate* (**14**), (E)-*Dodec*-9-*enyl Acetate* (**15**), (E)-*Tetradec*-9-*enyl Acetate* (**16**), (E)-*Tetradec*-11-*enyl Acetate* (**17**), *and* (E)-*Hexadec*-11-*enyl Acetate* (**18**).—All the (*E*)-alkenyl acetates (**14**)—(**18**) were prepared with isomeric purity higher than 99.5%, according to the procedure followed for the corresponding (*Z*)-alkenyl acetates, starting with (*E*)-1-phenylthio-ω-tetrahydropyranyloxyalk-1-enes (**22**)—(**24**). (*E*)-Dodec-7-enyl acetate (**14**), obtained from (**22**) and n-C_4H_9MgBr (81% yield), had b.p. 88—90 °C/0.08 Torr (lit.,[9c] 79—80 °C/0.04 Torr). The spectral data were identical with those of a commercial authentic sample. (*E*)-Dodec-9-enyl acetate (**15**), obtained from (**23**) and C_2H_5MgBr (79% yield), had b.p. 97—98 °C/0.08 Torr [lit.,[13f] 90 °C (bath)/0.1 Torr]. The spectral data were identical with those of a commercial authentic sample. (*E*)-Tetradec-9-enyl acetate (**16**), obtained from (**23**) and n-C_4H_9MgBr (74% yield), had b.p. 111—112 °C/0.08 Torr (lit.,[9c] 100 °C/0.05 Torr). ^1H N.m.r. spectral data were as previously reported;[9c] $\nu_{max.}$ 1 740, 1 235, 1 040, and 965 cm^{-1}; *m*/*z* 194 (3), 138 (2), 124 (6), 110 (16), 96 (44), 82 (69), 67 (68), 55 (100), and 43 (95). (*E*)-Tetradec-11-enyl acetate (**17**), obtained from (**24**) and C_2H_5MgBr (74% yield), had b.p. 106—107 °C/0.08 Torr (lit.,[9c] 98 °C/0.06 Torr). The spectral data were identical with those of a commercial authentic sample. (*E*)-Hexadec-11-enyl acetate (**18**) obtained from (**24**) and n-C_4H_9MgBr (78% yield) had b.p. 127—128 °C/0.08 Torr; $\nu_{max.}$ 1 740, 1 235, 1 040, and 965 cm^{-1}; δ_H 5.32 (m, 2 H), 3.98 (t, 2 H), 2.2—1.8 (br, 4 H), 1.95 (s, 3 H), 1.8—1.1 (br, 20 H), and 0.90 (t, 3 H); *m*/*z* 222 (19), 138 (10), 124 (17), 110 (32), 96 (66), 82 (73), 67 (59), 55 (77), and 43 (100).

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