nitrogen or argon. The sample was then degassed with five freeze–thaw cycles under reduced pressure (ca. 0.05 mmHg) and then sealed while cold. The tube was heated at 170–180 °C for a 2- to 3-h period, allowed to cool to room temperature, and opened. Solvent was removed in vacuo and the residue was purified by flash column chromatography over silica gel.

(±)-4-Methyl-1-(1-methyl-2-methylenecyclopentyl)-3-cyclohexene-1-carboxaldehyde: Trichodienal (6T) and Bazzanenal (6B). A 40:60 *E*:*Z* mixture of **5** was thermally rearranged at 180 °C for 2.0 h to give the crude aldehydes **6T** and **6B** in a 40:60 ratio, as determined by analysis of the ^{1}H NMR spectrum. Purification over silica gel (10% ethyl acetate/hexanes) afforded a spectroscopically pure mixture of the two aldehydes in 78% yield.

Spectral data: 200-MHz ^{1}H NMR δ 9.80 (s, 0.6 H, aldehydic), 9.60 (0.4 H, aldehydic), 5.40 (br s, 1 H, H-3), 5.05 (br s, 1 H, *exo*-vinyl), 4.78 (br s, 1 H, *exo*-vinyl), 2.5–1.4 (m, 12 H, H-2, H-5, H-6, cyclopentyl CH_2), 1.60 (br s, 3 H, allylic methyl), 1.00 (s, 3 H, methyl); IR 1725 cm^{-1} (s, C=O).

(±)-1,4-Dimethyl-1-(1-methyl-2-methylenecyclopentyl)-1-cyclohexene: Trichodiene (1) and Bazzanene (2). Method A. A 20:80 mixture of allyl vinyl ethers (*E*)-**5** and (*Z*)-**5** (70 mg; 0.3 mmol) in 0.5 mL of dry 1-butanol was placed in an base-washed glass ampule (7 mm o.d., 5 mm i.d.), under dry argon at room temperature. To this was added a solution containing anhydrous hydrazine (32 mg, 1.0 mmol) and potassium *tert*-butoxide (80 mg, 0.7 mmol) in 0.5 mL of 1-butanol, to give a homogeneous yellow solution. The sample was then degassed with five successive freeze–thaw cycles and sealed at ca. 0.1 mmHg pressure. The tube was heated in an oil bath at 200–210 °C for 3.5–4.0 h, during which time the reaction mixture became clear. After cooling, the tube was opened and and its contents were diluted with 5 mL of pentane. The separated organic layer was washed 4 times with 5-mL portions of brine, dried ($MgSO_4$), and concentrated in vacuo to yield a light yellow oil. Chromatography over 5 g of silica gel (pentane) afforded a fraction containing 50 mg (82%) of a 40:60 mixture of natural products **1** and **2**.[5]

Spectral data: 200-MHz ^{1}H NMR δ 5.30 (m, 1 H, C=CH), 4.97 (br s, 1 H, exocyclic C=CH), 4.79 (br s, 0.6 H, *exo*-C=CH), 4.74 (br s, 0.4 H, *exo*-C=CH), 1.60 (br s, 3 H, allylic methyls), 2.3–1.2 (m, 12 H, ring protons), 1.05 (s, 1.2 H, CH_3), 1.02 (s, 1.8 H, CH_3), 0.86 (s, 1.2 H, CH_3), 0.84 (s, 1.8 H, CH_3); IR 1638 cm^{-1} (m, C=C); MS (70 eV), *m/e* 204 (M^+).

Method B. Subjection of a 33:67 mixture of aldehydes **6T** and **6B** to the conditions of method A, and on a similar scale, yielded a 33:67 mixture of trichodiene and bazzanene in 80% yield.

Insect Sex Pheromones. Stereospecific Synthesis of (*E*)-13,13-Dimethyl-11-tetradecen-1-ol Acetate via a Thiophenol-Mediated Olefin Inversion

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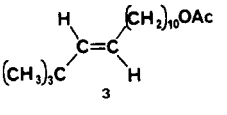
Received August 2, 1985

In the course of our study on structure–activity relationships between analogues of the sex pheromone of the European corn borer *Ostrinia nubilalis* (Hübner),[1] the geometrical isomers of 13,13-dimethyl-11-tetradecen-1-ol acetate were required. Coates and Johnson[2] described the synthesis of the cis isomer of an analogous olefin, (2*Z*,6*Z*)-1-(benzyloxy)-3,8,8-trimethyl-2,6-nonadiene, by the Wittig reaction between pivaldehyde and the appropriate phosphorane. They found, however, that even under Schlosser–Wittig conditions,[3] which normally favor formation of *trans*-olefins, in their special case involving a sterically hindered aldehyde, only the cis isomer could be obtained. Coates and Johnson prepared the (2*Z*,6*E*) isomer via a multistage procedure that involved reduction of the *trans*-6,7-enol phosphate with lithium in liquid ammonia as the final olefin-forming step. As an alternative to their approach, we explored the acetylenic route[4] to prepare the two desired compounds.

Alkylation of lithium *tert*-butylacetylide by [(10-bromodecyl)oxy]tetrahydro-2*H*-pyran was carried out in THF/hexamethylphosphorictriamide (HMPT) solvent. Conversion of the crude alkylation product by heating with a 10:1 acetic acid/acetic anhydride mixture gave 13,13-dimethyl-11-tetradecyn-1-ol acetate (**1**). Semihydrogenation of **1** in the presence of P_2–nickel[5] yielded (*Z*)-13,13-dimethyl-11-tetradecen-1-ol acetate (**2**).

Two convenient methods are available for the stereospecific trans reduction of isolated triple bonds: reduction with $LiAlH_4$ in refluxing diglyme;[6] reduction with Na in liquid ammonia/THF.[4] However, when **1** was refluxing in diglyme with excess $LiAlH_4$ for 12 h, starting material was recovered quantitatively after reacetylation. Reduction with Na in liquid NH_3/THF led only to partial reduction of **1**; ca. 70% of starting material remained after 8 h of contact time with excess Na. GC/MS analysis showed that the product now contained other positional isomers resulting from double-bond migrations. Although a mixture of *trans*-olefinic products could be readily separated by HPLC on an $AgNO_3$-impregnated silica column from acetylenic starting material, this mixture was not amenable to further purification.

As a third alternative for the preparation of the desired trans compound, the equilibration of the corresponding cis isomer in the presence of thiophenol[7] was investigated. At this point, this route looked attractive because separation by HPLC of the expected cis/trans equilibrium mixture would present no problem. When neat **2** was heated with a catalytic amount of thiophenol in a sealed tube to 100 °C,[8] slow isomerization was observed, but equilibrium had not been reached even after 24 h. Increasing the reaction temperature to 140 °C led to a 4:96 cis to trans mixture after 24 h. Refluxing a mixture of **2** and thiophenol in xylene in an inert atmosphere for *1* week led to a crude product that was essentially pure **3**. The

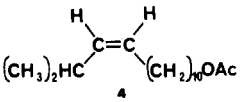


reaction time could be shortened if air was bubbled through the refluxing solution. We supposed that air oxidation must have increased the benzenethiyl radical concentration, leading, in turn, to an increased rate of

(1) Klun, J. A.; Chapman, O. L.; Mattes, K. C.; Wojtkowski, P. W.; Beroza, M.; Sonnet, P. E. *Science (Washington, D.C.)* **1973**, *181*, 661.
(2) Coates, R. M.; Johnson, M. W. *J. Org. Chem.* **1980**, *45*, 2685.
(3) Schlosser, M.; Christmann, K. F. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 126.
(4) Schwarz, M.; Waters, R. M. *Synthesis* **1972**, 567.
(5) Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553.
(6) (a) Slaugh, L. H. *Tetrahedron* **1966**, *22*, 1741. (b) Rossi, R.; Carpita, A. *Synthesis* **1977**, 561.
(7) Sgoutas, D. S.; Kummerow, F. A. *Lipids* **1969**, *4*, 283.
(8) Henrick, C. A.; Willy, W. E.; Baum, J. W.; Baer, T. A.; Garcia, B. A.; Mastre, T. A.; Chang, S. M. *J. Org. Chem.* **1975**, *40*, 1.

isomerization. This was borne out by experiments using 2,2′-azobis(2-methylpropanenitrile) (AIBN). We found that neat **2**, when heated with 16% by weight of thiophenol and 8% by weight of AIBN at 80 °C for 0.5 to 1 h, was completely isomerized to **3**. When the isomerization was carried out in refluxing benzene, nearly complete isomerization took place in 2 h. Interestingly, heating in toluene at 100 °C did not lead to complete isomerization, even after adding additional AIBN, presumably due to the much shorter life time of the 2-cyanopropyl radical at that temperature.

The complete inversion of geometry that we have observed merits some comment. Thiophenol-catalyzed equilibrations are thought to proceed via the addition of a benzenethiyl radical to the double bond, forming a new radical that decomposes to either *cis*- or *trans*-olefin.[8] The ratio of cis to trans products is an expression of the relative thermodynamic stability of the *cis*-or *trans*-olefins. In the previously reported cases, this ratio is ca. 20:80 cis to trans.[7,8] The greater than 99% isomerization to the trans compound in the *tert*-butyl case must be caused by the much greater thermodynamic stability of that isomer. As a corollary, the isomerization of (*Z*)-13-methyl-11-tetradecen-1-ol acetate (**4**) (see the Experimental Section) was also studied. The isomerization of this compound proceeded readily even without AIBN. Equilibrium was reached at a trans to cis ratio of 87:13. This ratio was intermediate to the 80:20 trans to cis ratio obtained with a nonhindered double bond flanked by two methylene groups[8,9] and the *tert*-butyl case studied.



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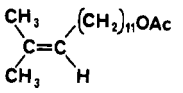
During equilibration of **4**, the formation of up to 30% of 13-methyl-12-tetradecen-1-ol acetate (**5**) was observed.



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The structure of this compound was verified by ozonolysis of the equilibrated mixture and comparison of GLC retention times of authentic 11-oxoundecan-1-ol acetate and 12-oxododecan-1-ol acetate with the aldehydes formed by the ozonolysis. Authentic **5**, prepared by a Wittig reaction between acetone and (12-hydroxydodecylidene)triphenylphosphorane and conversion to the acetate, had coincident GLC retention times with the rearrangement product in both polar and nonpolar capillary columns. The rearrangement of **4** to **5** must have resulted from hydrogen abstraction and radical formation at the methine carbon with subsequent allylic rearrangement. This shift of the double bond to adjacent methylene carbons[7,8] has not been observed.

In conclusion, we have shown that trans-substituted olefins, containing a quaternary carbon adjacent to the double bond and that cannot be readily prepared by the Wittig reaction or by chemical reduction of the corresponding acetylenes, may be stereospecifically synthesized by inversion of the readily available *cis*-olefins using thiophenol–AIBN. Also, double-bond migration owed to an allylic shift was found to be an important side reaction in the thiyl-mediated equilibration of an olefin having a methine carbon next to the double bond.

(9) Equilibration of a mixture of (*E*)- and (*Z*)-13,13-dimethyl-10-tetradecen-1-ol acetate (25:75) using thiophenol and AIBN also gave the "normal" 80:20 trans to cis mixture of isomers.

Experimental Section[10]

IR spectra were recorded on a Perkin-Elmer Model 1320 instrument using 5% solutions in CCl_4. ^1H NMR and ^{13}C NMR spectra were recorded in parts per million (δ units) on a GE NMR QE-300 spectrometer using C_6D_6 solutions with Me_4Si as an internal standard. GC/MS data were obtained at 70 eV on a Finnigan 4500 instrument using a 60 m × 0.25 mm i.d. fused-silica DB-1 capillary column. GLC analyses were carried out on a Shimadzu GL-9 instrument equipped with a 60 m × 0.25 mm i.d. fused-silica DB-1 capillary column and a Hewlett-Packard 5880A instrument equipped with a 60 m × 0.25 mm i.d. fused-silica Supelco-wax 10 capillary column. Preparative HPLC was carried out on a Waters Associates instrument equipped with two stainless-steel columns, 25 cm × 10 mm i.d. in series and packed with 10-μm silica impregnated with 20% $AgNO_3$ using toluene at a flow rate of 4 mL/min as the eluant. Elemental analyses were performed by Galbraith Laboratories.

THF and diglyme were distilled from $LiAlH_4$, and HMPT was vacuum distilled from CaH_2 prior to use. All reactions, unless otherwise stated, were run in an inert atmosphere.

10-Bromodecan-1-ol was prepared as described by Camps et al.[11] A solution of 1,10-decanediol (100 g, 0.57 mol) in 48% HBr (600 mL, 5.3 mol) was placed in a liquid–liquid extraction apparatus and heated to 85 °C. The reaction mixture was continuously extracted with heptane (700 mL) for 3 h. To free the product from contaminating 1, 10-dibromodecane, the heptane solution, after cooling, was diluted with pentane (300 mL) and placed in a freezer (−20 °C), and the product was allowed to crystallize. The supernatant was decanted and the solid redissolved in pentane (1 L) and allowed to crystallize (−20 °C). The crystalline product was filtered by a pressure filter funnel surrounded by a cooling jacket (−20 °C) and washed with precooled (−20 °C) pentane. The product was distilled under reduced pressure to yield 105 g (78%) of 10-bromodecan-1-ol: bp 120–122 °C (0.10 mm) [lit.[11] bp 99–101 °C (0.07 mm)].

2-[(10-Bromodecyl)oxy]tetrahydro-2*H*-pyran. To a stirred, ice-cold solution of 10-bromodecan-1-ol (74 g, 0.31 mol) and 1 mL of concentrated HCl in 100 mL of diethyl ether was added dropwise dihydropyran (42 g, 0.50 mol). The reaction, monitored by TLC, was brought to completion by refluxing overnight. The reaction mixture was diluted with pentane (100 mL), extracted with saturated Na_2CO_3(aq) and brine, and dried (K_2CO_3). After evaporation of the solvent and excess dihydropyran, the product was distilled from a small amount of $NaHCO_3$(s), to yield 85 g (85%) of product: bp 130–134 °C (0.10 mm) [lit.[12] bp 140 °C (0.25 mm)].

13,13-Dimethyl-11-tetradecyn-1-ol Acetate (1). To a stirred solution of *tert*-butylacetylene (2.9 g, 0.035 mol) in THF (25 mL) was added methyllithium in ether (37 mL, 1.1 M, 0.040 mol) while the temperature was kept below 15 °C. 2-[(10-Bromodecyl)-oxy]tetrahydro-2*H*-pyran (11.2 g, 0.035 mol) in HMPT (50 mL) was added dropwise while the temperature was kept below 20 °C. The mixture was allowed to come to room temperature and was worked up after 1 h by pouring into ice water and extracting 3× with pentane. The organic layer was washed twice with water and once with brine and dried (Na_2SO_4). After removal of the solvent, the product was heated to 80 °C for 3 h in a 10:1 mixture of acetic acid/acetic anhydride (35 mL). After cooling, the reaction mixture was diluted with pentane and ice water and stirred for 0.5 h in an ice bath. The organic layer was separated and the aqueous layer extracted twice with pentane. The combined organic extracts were washed twice with water and with brine and dried (Na_2SO_4). After removal of the solvent, the residue was distilled to yield 7.8 g (80%) of **1**: bp 125 °C (bath) (0.025 mm) (short-path still); IR ν 2966 (s), 2927 (s), 2857 (s), 1733 (s), 1385 (w), 1358 (m), 1258 (sh), 1324 (s), 1207 (sh), 1033 (m) cm^{-1}; ^1H NMR δ 1.18 (s, 9 H, $(CH_3)_3C$), 1.23 (br s, chain CH_2), 1.45 (m,

(10) Mention of a commercial product does not constitute endorsement of that product by the USDA.

(11) Camps, F.; Casamor, J. M.; Coll, J.; Guerrero, A.; Riba, M. *Org. Prep. Proc. Int.* **1983**, *15*, 63.

(12) Mattes, K. C. Ph.D. Dissertation, Iowa State University, Ames, IA, 1975.

2 H, β-OCH_2CH_2), 1.76 (s, 3 H, CH_3CO_2), 2.10 (t, 2 H, $CH_2C{\equiv}C$, J = 7 Hz), 3.97 (t, 2 H, CH_2OCOCH_3, J = 7 Hz); ^{13}C NMR δ 19.02, 20.53, 26.22, 27.54, 29.0–30.0, 31.62, 64.30, 78.80, 88.92, 169.87; GC/MS m/e (relative intensity) 280 (M^+, 0.7), 220 (M − 60, 0.3), 135 (11), 121 (14), 110 (100), 109 (17), 107 (16), 96 (21), 95 (47), 93 (17), 81 (27), 79 (11), 67 (11), 61 ($CH_3COOH_2^+$, 1). Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 77.34; H, 11.24.

13-Methyl-11-tetradecyn-1-ol Acetate. This compound was prepared in the same manner as 1 from isopropylacetylene and methyllithium to give a 76% yield: bp 120 °C (bath) (0.025 mm) (short-path still); IR ν 2966 (s), 2928 (s), 2856 (s), 1733 (s), 1380 (w), 1359 (m), 1314 (w), 1233 (s), 1033 (m) cm^{-1}; ^1H NMR δ 1.12 (d, 6 H, $(CH_3)_2CH$, J = 7 Hz), 1.18 (br s, chain CH_2), 1.76 (s, 3 H, CH_3CO_2), 2.12 (t, 2 H, $CH_2C{\equiv}C$, J = 6 Hz), 2.49 (m, 1 H, $(CH_3)_2CHC{\equiv}C$), 3.98 (t, 2 H, CH_2OCOCH_3, J = 7 Hz); ^{13}C NMR δ 19.11, 20.55, 20.99, 23.71, 26.26, 29.0-29.8, 64.36, 79.57, 86.09, 169.98; GC/MS m/e (relative intensity) 206 (M − 60, 0.06), 96 (38), 95 (21), 93 (16), 83 (13), 82 (100), 81 (38), 79 (19), 69 (16), 67 (43), 61 ($CH_3COOH_2^+$, 3). Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.31; H, 11.59.

(*Z*)-13,13-Dimethyl-11-tetradecen-1-ol Acetate (2). Compound 1 was reduced according to Brown and Ahuja[5] using P_2–Ni catalyst. In a 100-mL flask with stoppled sidearm was placed $Ni(OAc)_2{\cdot}4H_2O$ (0.10 g, 0.40 mmol) and ethanol (20 mL), and the flask was attached to an atmospheric pressure hydrogenator. Under a hydrogen atmosphere was added sequentially via syringe a 1 M $NaBH_4$ solution in ethanol (0.4 mL, 0.4 mmol) and a 50% v/v solution of ethylenediamine/ethanol (0.1 mL, 0.8 mmol). The resultant catalyst suspension was magnetically stirred in the hydrogen atmosphere for 15 min, 1 (0.90 g, 3.2 mmol) was injected, and the theoretical amount of hydrogen was taken up in ca. 2 h. The reaction mixture was diluted with 50 mL of water containing 1 mL of glacial acetic acid and extracted 3× with pentane. The organic layer was washed twice with water and once with brine and dried (Na_2SO_4). After evaporation of the pentane, the product was distilled: bp 120 °C (bath) (0.025 mm) (short-path distillation); 0.67 g (74%).

An analytical sample was further purified by HPLC and redistilled: IR ν 2996 (m), 2926 (s), 2855 (s), 1732 (s), 1644 (w), 1383 (m), 1359 (s), 1233 (s), 1204 (w, sh), 1035 (m) cm^{-1}; ^1H NMR δ 1.13 (s, 9 H, $(CH_3)_3C$), 1.21 (br s, 16 H, chain CH_2), 1.77 (s, 3 H, CH_3CO_2), 2.20 (m, 2 H, $CH_2C{=}C$), 3.97 (t, 2 H, CH_2OCOCH_3, J = 7 Hz), 5.21 (dt, 1 H, $CH{=}CC(CH_3)_3$, J = 7 Hz, 12 Hz), 5.36 (dt, 1 H, $C{=}CHC(CH_3)_3$, J = 1 Hz, 12 Hz); ^{13}C NMR δ 20.53, 26.24, 28.8–31.4, 33.19, 64.26, 129.35, 139.69, 169.76; GC/MS m/e (relative intensity) 282 (M^+, 0.5), 222 (M − 60, 7), 166 (31), 123 (16), 110 (15), 109 (25), 97 (22), 96 (23), 95 (37), 84(24) 83 (100), 82 (29), 81 (28), 70 (29), 69 (55), 68 (11), 67 (24), 61 ($CH_3COOH_2^+$, 6). Anal. Calcd for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13. Found: C, 76.59; H, 11.88.

(*Z*)-13-Methyl-11-tetradecen-1-ol Acetate (4). P_2–Ni reduction of 13-methyl-11-tetradecyn-1-ol acetate was carried out in the same manner as the reduction of 1. Thus, 13-methyl-11-tetradecyn-1-ol acetate (1.7 g, 6.4 mmol) was reduced with P_2–Ni catalyst prepared from $Ni(OAc)_2{\cdot}4H_2O$ (0.2 g, 0.8 mmol), $NaBH_4$ (0.8 mL, 1 M solution in ethanol, 0.8 mmol), and ethylenediamine (0.2 mL, 50% v/v solution in ethanol, 1.5 mmol) in 50 mL ethanol. The reduction was complete in ca. 45 min. Workup and distillation yielded 1.5 g (87%) of 4: bp 120 °C (bath) (0.025 mm) (short-path still). The analytical sample was further purified by HPLC and redistilled: IR ν 2998 (m), 2954 (s), 2924 (s), 2856 (s), 1736 (s), 1384 (m), 1360 (s), 1235 (s), 1163 (w), 1099 (w), 1036 (s); ^1H NMR δ 0.96 (d, 6 H, $(CH_3)_2CH$, J = 7 Hz), 1.19 (br s, chain CH_2), 1.74 (s, 3 H, CH_3CO_2), 2.05 (m, 2 H, $CH_2C{=}C$), 2.61 (m, 1 H), $(CH_3)_2CHC{=}C$), 3.97 (t, 2 H, CH_2OCOCH_3, J = 7 Hz), ca. 5.24 (complex m, 2 H, olefinic); ^{13}C NMR δ 20.54, 23.41, 26.27, 26.84, 27.73, 29.0–30.0, 30.35, 64.40, 128.34, 137.73, 170.0; GC/MS m/e (relative intensity) 268 (M^+, 0.4), 208 (M − 60, 23), 124 (15), 123 (15), 110 (22), 109 (29), 97 (25), 96 (59), 95 (65), 83 (36), 82 (100), 81 (51), 70 (12), 69 (73), 68 (31), 67 (41), 61 ($CH_3COOH_2^+$, 11). Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.17; H, 12.34.

(*E*)-13-Methyl-11-tetradecen-1-ol Acetate. To a magnetically stirred solution of $LiAlH_4$ (1.5 g, 40 mmol) in 75 mL of diglyme was added dropwise 13-methyl-11-tetradecyn-1-ol acetate (2.66 g, 10 mmol). After the addition was complete, the mixture was refluxed for 20 h. The reaction mixture was then cooled in an ice bath, and excess $LiAlH_4$ was decomposed by the addition of water (1.5 mL), 15% NaOH (1.5 mL), and water (6 mL). The mixture was filtered, and the filtrate diluted with pentane and extracted twice with water and once with brine and dried (Na_2SO_4). Evaporation of the pentane yielded the crude alcohol that was directly converted to acetate by treatment with acetic anhydride (20 mL) and pyridine (2 mL). The reaction mixture was warmed for 1 h to 80 °C to complete the acetylation. After cooling, the excess acetic anhydride was decomposed with ice water and the product extracted with pentane. The pentane layer was washed twice with water and once with brine and dried (Na_2SO_4). After evaporation of the pentane, the (*E*)-13-methyl-11-tetradecen-1-ol acetate was distilled at 110 °C (bath) (0.025 mm) (short-path still) to yield 2.47 g (92%). GLC of the product revealed that it was contaminated with ca. 8% of starting alkyne. A sample for analysis was purified by HPLC and redistilled: IR ν 3020 (w), 2955 (s), 2927 (s), 2856 (s), 1733 (s), 1381 (w), 1361 (s), 1235 (s), 1035 (m), 968 (m) cm^{-1}; ^1H NMR δ 0.97 (d, 6 H, $(CH_3)_2CH$, J = 7 Hz), 1.21 (br s, chain CH_2), 1.77 (s, 3 H, CH_3CO_2), 1.98 (m, 2 H, $CH_2C{=}C$), 2.22 (complex m, 1 H, $(CH_3)_2CHC{=}C$), 3.97 (t, 2 H, CH_2OCOCH_3, J = 7 Hz), 5.38 (complex m, 2 H, olefinic); ^{13}C NMR δ 20.51, 22.90, 26.27, 29.0-30.1, 31.42, 32.97, 64.26, 127.51, 137.77, 169.73; GC/MS m/e (relative intensity) 268 (M^+, 0.4), 208 (M − 60, 19), 124 (13), 123 (15), 110 (20), 109 (27), 97 (23), 96 (55), 95 (62), 83 (35), 82 (100), 81 (48), 70 (11), 69 (72), 68 (31), 67 (39), 61 ($CH_3COOH_2^+$, 10). Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.07; H, 12.15.

(*E*)-13,13-Dimethyl-11-tetradecen-1-ol Acetate (3). A mixture of 2 (0.1 g, 0.4 mmol), thiophenol (0.021 g, 0.19 mmol), and AIBN (0.01 g, 0.06 mmol) was heated in a capped vial to 80 °C. The olefin inversion was monitored by GC, and after 0.5 h less than 1% of 2 remained. The reaction mixture was subjected directly to vacuum distillation to give essentially pure 3: bp 120 °C (bath) (0.025 mm) (short-path still) in quantitative yield. A sample for analysis was further purified by HPLC and redistilled: IR ν 3052 (w), 2952 (s), 2926 (s), 2856 (s), 1734 (s), 1385 (w), 1359 (m), 1232 (s), 1148 (w), 1033 (m), 969 (m); ^1H NMR δ 1.02 (s, 9 H, $(CH_3)_3C$), 1.19 (br s, chain CH_2), 1.74 (s, 3 H, CH_3CO_2), 2.00 (m, 2 H, $CH_2C{=}C$), 3.94 (t, 2 H, CH_2OCOCH_3, J = 7 Hz), 5.33 (dt, 1 H, $CH{=}CC(CH_3)_3$, J = 6 Hz, 16 Hz), 5.48 (d, 1 H, $C{=}C$-$HC(CH_3)_3$, J = 16 Hz); ^{13}C NMR δ 20.52, 26.25, 29.0-30.0, 32.86, 33.11, 64.30, 125.08, 141.69, 169.85; GC/MS m/e (relative intensity) 282 (M^+, 0.4), 222 (M − 60, 8), 166 (37), 124 (11), 123 (17), 110 (18), 109 (28), 97 (23), 96 (28), 95 (44), 84 (21), 83 (100), 82 (36), 81 (34), 70 (25), 69 (66), 68 (13), 67 (28), 61 ($CH_3COOH_2^+$, 7). Anal. Calcd for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13. Found: C, 76.80; H, 12.11.

The conversion of 2 to 3 was also carried out in refluxing benzene using the same quantities of reactant and reagents in 10 mL of solvent. After 2 h, ca. 1% of 2 remained. Upon the addition of a small crystal of AIBN and further reflux for 2 h, no more 2 was detectable in the reaction mixture. Removal of the benzene and distillation as above yielded pure 3.

Equilibration of 4. A mixture of 4 (0.1 g, 0.4 mmol), thiophenol (0.021 g, 0.19 mmol), AIBN (0.01 g, 0.06 mmol) was heated in a capped vial to 80 °C. The equilibration was monitored by GLC; after 0.5 h the trans content was 87%. Addition of a final 10 mg of AIBN and continued heating for 1 h did not change the cis to trans ratio. Equilibration of 4 in refluxing benzene in the presence of thiophenol and AIBN gave essentially the same equilibrium in 4 h, after addition of fresh AIBN at 1 h. A rearrangement product that eluted after the cis and trans isomers, accounting for ca. 30% of starting material, was observed in both equilibrations.

When (*Z*)-11-tetradecen-1-ol acetate was subjected to the same conditions, an equilibrium mixture of the cis and trans isomers in the ratio of 80:20 was obtained within 0.5 h.

Identification of Rearrangement Product Formed during Equilibration of 4. GC/MS revealed that the new peak was an acetate of the same molecular weight as 4 (strong m/e M − 60 and m/e 61 peaks). Ozonolysis of the mixture gave two compounds in a 70:30 ratio. These compounds had retention times identical with those of the ozonolysis products of (*Z*)-11-tetradecen-1-ol acetate, i.e. 11-oxoundecan-1-ol acetate, and (*Z*)-12-tetradecen-1-ol acetate,[13] i.e. 12-oxododecan-1-ol acetate, re-

spectively. These results indicated that the rearranged product was 13-methyl-12-tetradecen-1-ol acetate (5).

13-Methyl-12-tetradecen-1-ol Acetate (5). (12-Hydroxydodecyl)triphenylphosphonium bromide, prepared according to Schaub et al.[14] (3.1 g, 5.9 mmol), was suspended in THF (50 mL). Methyllithium (9.1 mL, 1.5 M in ether, 14 mmol) was added dropwise while the mixture was kept below 10 °C. After 0.5 h, excess acetone was added. The reaction mixture was allowed to stand at room temperature for 2 h. A small amount of water was added, and the ether and THF were removed at reduced pressure. The residue was extracted with pentane, washed twice with water and brine, and dried (Na_2SO_4). After evaporation of the pentane, the residue was acetylated with acetic anhydride/pyridine in the usual manner. Workup and distillation yielded 5: bp 120 °C (0.025 mm) (bath temperature) (short-path still) in a 20% yield. The analytical sample was purified by HPLC: IR ν 2922 (s), 2855 (s), 1733 (s), 1360 (m), 1233 (s), 1035 (m) cm^{-1}; ^1H NMR δ 1.20 (br s, chain CH_2), 1.58 (s, 3 H, *cis*-$CH_3C{=}C$), 1.68 (s, 3 H, *trans*-$CH_3C{=}C$), 1.74 (s, 3 H, CH_3CO_2), 3.98 (t, 2 H, CH_2OCOCH_3, J = 7 Hz), 5.21 (t, 1 H, olefinic, J = 7 Hz); ^{13}C NMR δ 17.72, 20.53, 25.87, 26.31, 28.5-30.4, 64.35, 125.41, 130.93, 169.92; GC/MS *m/e* (relative intensity) 268 (M^+, 2), 208 (M - 60, 13), 124 (11), 123 (11), 110 (17), 109 (21), 97 (20), 96 (49), 95 (54), 83 (29), 82 (100), 81 (36), 70 (12), 69 (97), 68 (35), 67 (35), 61 ($CH_3COOH_2^+$, 10). Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.03; H, 11.79.

The compound had a congruent mass spectrum and identical GLC retention times on both polar and nonpolar columns with the rearrangement product of 4.

Acknowledgment. We thank E. D. Devilbiss and B. A. Leonhardt of our laboratory for mass spectra.

(13) Li, Z.; Schwarz, M. *Scientia Sinica (Ser. B)* **1984**, *27*, 679.
(14) Schaub, B.; Blaser, G.; Schlosser, M. *Tetrahedron Lett.* **1985**, *26*, 307.

Anodic Trifluoromethylation of Acrylic Acid. Synthesis of Diethyl (2,2,2-Trifluoroethyl)malonate and Trifluorinated Analogues of Barbital and Amobarbital

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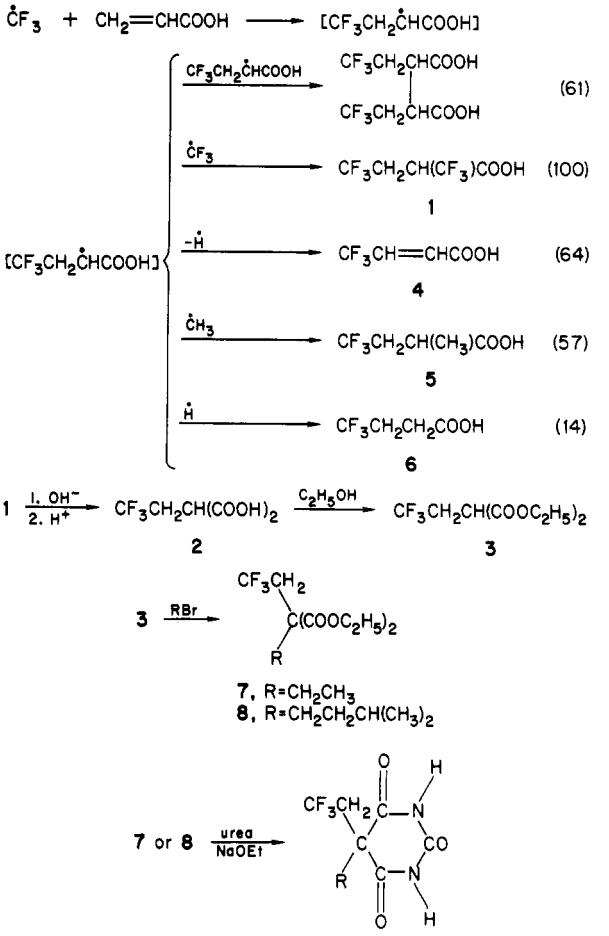
Received October 3, 1985

Oxidation of trifluoroacetate ions at an anode produces trifluoromethyl radicals which have been shown to react with olefinic cosolutes to yield more or less complex mixtures of mono- and bis-trifluoromethylated materials.[1-5] When it is fairly easy to isolate a pure product from such a mixture this may represent the most economical preparative procedure, especially for compounds containing functional groups that could not survive treatment with powerful fluorinating agents such as sulfur tetrafluoride. Several useful syntheses based on this approach have recently been described,[6-8] and a further one is presented here.

Scheme I



Other investigators had reported that electrolysis of trifluoroacetic acid with methyl or ethyl acrylate in aqueous acetonitrile or methanol gave mainly dimeric products and small amounts of esters of 2-(trifluoromethyl)-4,4,4-trifluorobutyric acid (1).[1,4] The latter is of interest in light of the fact that the trifluoromethyl groups of 2-trifluoromethyl carboxylic acids are apparently rapidly hydrolyzed in aqueous base to give the corresponding malonic acids.[9,10] It was therefore decided to seek conditions under which 1 would be a major electrolysis product and then attempt to convert it to the previously unknown and potentially very useful (2,2,2-trifluoroethyl)malonic acid (2). This was indeed accomplished, but the usefulness of 2 is severely limited because it loses carbon dioxide much more readily than malonic acid. It was, however, possible to obtain its diethyl ester (3) from which a number of new trifluoromethylated compounds can be prepared, including analogues of barbital and amobarbital. The key reactions are summarized in Scheme I.

Results and Discussion

Trial electrolyses were carried out with trifluoroacetic acid and acrylic acid, methyl acrylate, or higher esters of acrylic acid, in mixtures of water with several organic solvents, including methanol, acetonitrile, acetic acid, 2-

(1) Renaud, R. N.; Champagne, P. J. *Can. J. Chem.* **1975**, 53, 529.
(2) Renaud, R. N.; Champagne, P. J.; Savard, M. *Can. J. Chem.* **1979**, *57*, 2617.
(3) Brookes, C. J.; Coe, P. L.; Owen, D. M.; Pedler, A. E.; Tatlow, J. C. *J. Chem. soc., Chem. Commun.* **1974**, 323.
(4) Brooks, C. J.; Coe, P. L.; Pedler, A. E.; Tatlow, J. C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 202.
(5) Renaud, R. N.; Stephens, C. J.; Bérubé, D. *Can. J. Chem.* **1982**, *60*, 1687.
(6) Muller, N. *J. Org. Chem.* **1983**, *48*, 1370.
(7) Muller, N. *J. Org. Chem.* **1984**, *49*, 2826.
(8) Muller, N. *J. Org. Chem.* **1984**, *49*, 4559.
(9) Buxton, M. W.; Stacey, M.; Tatlow, J. C. *J. Chem. Soc.* **1954**, 366.
(10) Peters, H. M.; Ross, L. O.; Simon, Jr., R. L.; Hill, M. E. *J. Chem. Eng. Data* **1971**, *16*, 376.

0022-3263/86/1951-0263$01.50/0