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Stereoselective Synthesis of Sesquiterpene Lactones. Total Synthesis of (±)-Isotelekin

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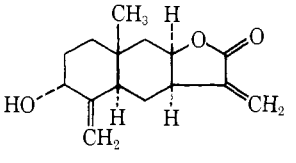
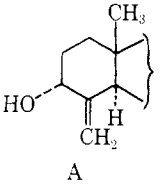
Abstract: A stereoselective total synthesis of racemic isotelekin (**1**) is described. Key steps in the synthesis are the introduction of the axial allylic alcohol moiety by base-promoted opening of an epoxide (**6**); introduction of a cis-fused five-membered ring lactone by enamine alkylation of a keto ester (**8**) followed by sodium borohydride reduction of the alkylated material (**9**); and introduction of an α-methylene group onto the lactone ring by a previously developed procedure involving Mannich reaction on an α-carbomethoxylactone (**12**) followed by quaternization and cleavage-elimination to give racemic isotelekin.

Isotelekin[1] (**1**) is one of a number of known lactone bitter principles belonging to the eudesmane class of sesquiterpenes.[2] An important structural feature of this compound is the α-methylene-γ-butyrolactone moiety which has attracted much synthetic interest recently[3] because of its occurrence in a wide variety of natural compounds having considerable biological activity as allergenic agents,[4] growth inhibitors,[5] antibacterial agents,[6] and antitumor agents.[7] This paper reports a stereoselective total synthesis of (±)-isotelekin.

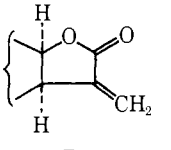
In approaching the synthetic problems presented by isotelekin, the molecule can be viewed as consisting of two parts, A and B. The approach to part A was to involve stereoselective epoxidation of an olefin from the side opposite



1

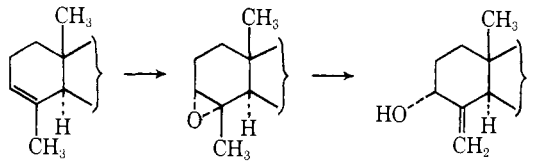


A

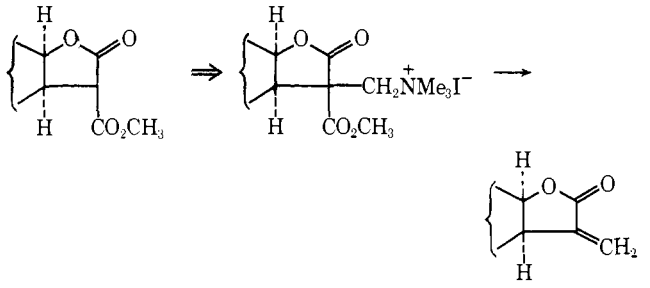


B

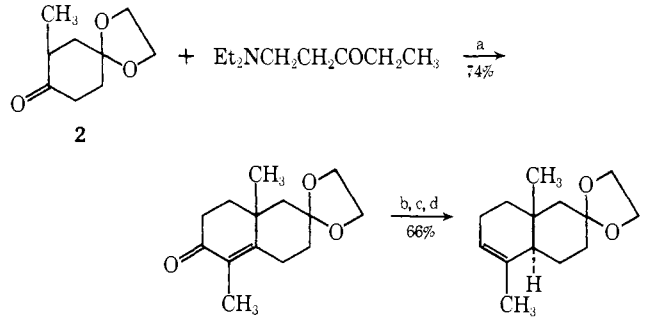
Scheme I



Scheme II

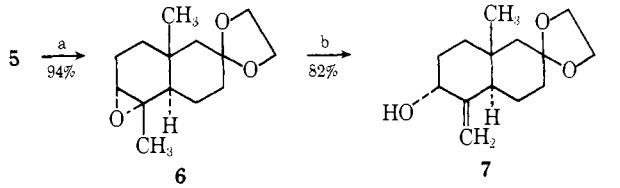


Scheme III



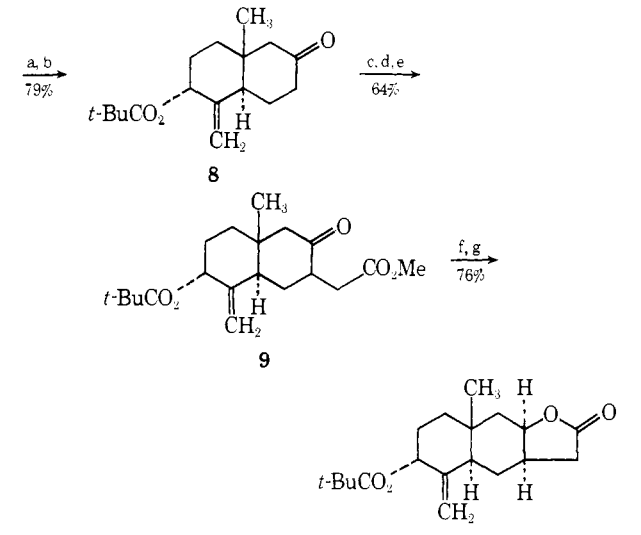
step a, Na; b, Li, NH_3(l); c, $(EtO)_2POCl$;
d, Li, $EtNH_2$, *t*-BuOH

Scheme IV



step a, *m*-$ClC_6H_4CO_2H$, CH_2Cl_2, 0°;
b, *i*-Pr_2NLi, Et_2O

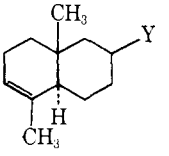
Scheme V



step a, *t*-BuCOCl, py; b, Me_2CO, *p*-TsOH; c, pyrrolidine;
d, $BrCH_2CO_2Me$; e, NaOAc, HOAc, H_2O;
f, $NaBH_4$, MeOH, 0°; g, dilute, HCl

the angular methyl group followed by base-promoted opening of the epoxide to give the axial allylic alcohol system (see Scheme I). Construction of part B was to follow a route previously developed in our laboratories[3i] for the introduction of the α-methylene-γ-butyrolactone moiety under mild conditions (see Scheme II).

Our initial synthetic goal was a compound (see C) whose structural features contained both a double bond in the



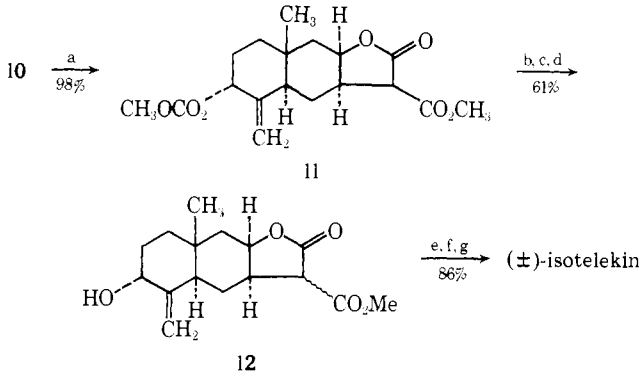
C

proper position for elaboration of the A portion and functionality at a position which would eventually allow introduction of groups leading to the lactone ring needed for elaboration of the B portion of isotelekin. The synthetic sequence to this desired intermediate is outlined in Scheme III. The starting material was 3-methyl-4-ethylenedioxycyclohexanone[8] (**2**)[9] which was subjected to an annelation reaction using 1-(*N,N*-diethylamino)-3-pentanone[10] **3** and sodium to give the crystalline octalone derivative **4** in 74% yield. Removal of the ketone group, transposition of the double bond, and establishment of the trans ring fusion were accomplished in a single sequence employing the very elegant procedure of Ireland.[11] Thus initial reduction of the α,β-unsaturated ketone with lithium in liquid ammonia gave a lithium enolate while generating the desired trans stereochemistry at the ring fusion.[12] Trapping of the enolate with diethyl chlorophosphite led to the expected enol phosphate which was directly reduced with lithium-ethylamine in the presence of *tert*-butyl alcohol to give the desired ketal-olefin **5** in 66% overall yield.

Elaboration of compound **5** into a system containing the A part of isotelekin was accomplished as shown in Scheme IV. Stereoselective epoxidation of the double bond was carried out using *m*-chloroperbenzoic acid in methylene chloride to give only ketal-epoxide **6** in 94% isolated yield.[13] Opening of the epoxide ring with lithium diisopropylamide in ether gave the desired crystalline ketal-allylic alcohol **7** in 82% yield. This product is consistent with the preference for elimination being primary ≫ secondary ≫ tertiary.[14]

Having successfully completed construction of the A portion of isotelekin, we turned to the problem of the B part. Transformation of compound **7** into the required lactone precursor is shown in Scheme V. The allylic alcohol moiety was first protected as the pivalate ester by treatment of compound **7** with pivaloyl chloride in pyridine, and then the crude ester was subjected to acetone in the presence of a catalytic amount of *p*-toluenesulfonic acid to cleave the ketal protecting group. The resulting crystalline keto-allylic ester **8** was obtained in 79% overall yield. Introduction of the acetic acid side chain was accomplished in a standard manner[15] by alkylation of the pyrrolidine enamine of compound **8** with methyl bromoacetate followed by mild hydrolysis to give keto diester **9** in 64% yield. Lactone formation was achieved by sodium borohydride reduction of compound **9** in cold methanol followed by acidic work-up giving

Scheme VI



step a, $NaH, (MeO)_2CO$; b, KOH, MeOH-H_2O; c, dilute, HCl
d, CH_2N_2, Et_2O; e, CH_2O, Me_2NH, Me_2NH·HCl, dioxane;
f, MeI; g, DMF, 80°

the desired crystalline lactone-ester **10** in 76% yield. The stereochemistry of the reduction to give the axial alcohol and subsequently the cis lactone is consistent with results obtained in similar systems.[15a,b,16] Also the nmr spectrum of compound **10** is consistent with the indicated stereochemistry of the lactone ring. The position of the chemical shift for the angular methyl group singlet in going from compound **9** to compound **10** has shifted to lower field, δ 0.70 and 0.84 ppm, respectively, indicating an interaction between the angular methyl group and the lactone oxygen. The chemical shift of the methine proton attached to the carbon bearing the lactone oxygen is also consistent with a cis-fused lactone ring having an equatorial hydrogen.[17]

Finally completion of the synthesis of (±)-isotelekin utilizing the procedure previously developed in our laboratories for the B portion is outlined in Scheme VI. Carbomethoxylation of the lactone in compound **10** was carried out using sodium hydride in dimethyl carbonate solvent. The desired reaction was accompanied by an unexpected transesterification to give crystalline lactone-diester **11** in 98% yield. Removal of the carbonate ester from the allylic alcohol moiety was accomplished by treatment of compound **11** with aqueous, methanolic potassium hydroxide followed by acidification and then esterification with ethereal diazomethane using an acidic work-up to give the crystalline hydroxy-lactone-ester **12** in 61% overall yield. Reaction of compound **12** with formaldehyde and dimethylamine gave a crude Mannich base which was quaternized in neat methyl iodide to give a crystalline quaternary ammonium salt. Heating this salt in dimethylformamide at 80° gave crystalline (±)-isotelekin in 86% yield (43% conversion, see Experimental Section). The synthetic material had identical solution infrared and nmr spectra with those of natural isotelekin, which was kindly provided by Professor Sorm (Institute of Organic Chemistry and Biochemistry, Czechoslovakia Academy of Science).

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60A instrument. Chemical shifts are quoted in parts per million downfield from internal tetramethylsilane. High resolution mass spectra were obtained with a Varian M-66 spectrometer. Combustion analyses were done by Chemalytics, Inc., Tempe, Ariz. Petroleum ether used was reagent grade with boiling range 30–60°. All reactions were carried out under a nitrogen atmosphere. Anhydrous sodium sulfate was used as the drying agent. Florisil (60–100 A) used for chromatography was purchased from Wilshire Chemical Co., Inc.

Ketoketal 4. Sodium metal (~0.2 g) was added to 80.7 g (0.474 mol) of 2-methyl-4-ethylenedioxycyclohexanone (**2**). The solution was heated at 50° until the metal reacted (~2 hr), and 37.3 g (0.237 mol) of amino ketone **3** was added. The mixture was heated slowly to 125°, and the temperature was maintained for 3 hr. The solution was cooled and acidified with 14.6 ml of glacial acetic acid, followed by 40 ml of ice–water. The mixture was quickly extracted with ether, and the combined extracts were washed with 10% sodium bicarbonate solution, water, and saturated sodium chloride solution and dried. The solvent was removed, and the residue was distilled to give 43.2 g of 2-methyl-4-ethylenedioxycyclohexanone (**2**) and 38.5 g (74% based on recvered ketone **2**) of ketoketal **4**; bp 131–135° (0.2 mm); ir (CCl_4) 1615 (C=C) and 1710 cm^{-1} (C=O); nmr (CCl_4) δ 0.8–3.0 (m, 10 H), 1.30 (s, 3 H), 1.70 (s, 3 H), and 3.80–4.00 ppm (m, 4 H). *Anal.* Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.28; H, 8.74.

Ketal-Olefin 5. To 5.00 g (21.2 mmol) of ketoketal **4** in 25 ml of ether was added 100 ml of liquid ammonia which was freshly distilled from sodium metal. Lithium metal was added until a blue color persisted for 1 hr. The ammonia was allowed to distil, and the ether solution was gently refluxed to ensure removal of all ammonia. Excess lithium metal was removed, and 18.6 g (108 mmol) of diethyl chlorophosphite in 25 ml of ether was added dropwise. The mixture was allowed to stir overnight at room temperature. To the white precipitate were added 100 ml of ethylamine, 2.0 ml of *tert*-butyl alcohol, and lithium metal until a blue color persisted for 1 hr. The ethylamine was allowed to evaporate, and excess lithium metal was removed. Sufficient water was added to dissolve the white precipitate, and the mixture was extracted with ether. The extracts were washed with water followed by saturated sodium chloride and dried. The solvent was removed, and the residue was chromatographed on Florisil to give 3.11 g (66%) of ketal-olefin **5**; ir (neat) 1635 cm^{-1} (C=C); nmr (CCl_4) δ 0.8–2.2 (m, 11 H), 0.90 (s, 3 H), 1.61 (s, 3 H), 3.83 (m, 4 H), and 5.28 ppm (m, 1 H); high resolution mass spectrum, *m/e* 222.1588 (calcd for $C_{14}H_{22}O_4$, 222.1620).

Ketal-Epoxide 6. To 50 ml of dichloromethane was added 4.46 g (20.1 mmol) of ketal-olefin **5**, and the mixture was cooled to 0°. To the stirred solution was added 5.17 g (30.1 mmol) of solid *m*-chloroperbenzoic acid, and the temperature was maintained at 0° for 10 hr. The mixture was allowed to come to room temperature, ether was added, and the solution was washed with 5% sodium hydroxide solution, water, and saturated sodium chloride solution. The extract was dried and concentrated. The residue was chromatographed on Florisil to give 4.44 g (94%) of ketal-epoxide **6**; nmr (CCl_4) δ 0.5–2.0 (m, 11 H), 0.87 (s, 3 H), 1.11 (s, 3 H), 2.71 (m, 1 H), and 3.78 ppm (m, 4 H); high resolution mass spectrum, *m/e* 238.1574 (calcd for $C_{14}H_{22}O_3$, 238.1569).

Ketal-Allylic Alcohol 7. To 3.93 ml (31.8 mmol) of diisopropylamine in 400 ml of ether was cautiously added 19.8 ml of 1.6 *M* *n*-butyllithium (31.8 mmol), and the mixture was stirred for 30 min at room temperature. A solution of 3.03 g (12.7 mmol) of ketal-epoxide **6** in 10 ml of ether was added, and the mixture was stirred for 24 hr at room temperature. Water was added, and the solution was extracted with ether. The combined extracts were washed with water and saturated sodium chloride solution, dried, and concentrated. The residue was chromatographed on Florisil to yield 2.62 g (86%) of ketal-allylic alcohol **7** as a white solid. An analytical sample was recrystallized from an ether–petroleum ether mixture: mp 76–78°; ir (CCl_4) 910 (C=CH_2), 1640 (C=C), and 3610 cm^{-1} (O–H); nmr (CCl_4) δ 0.6–2.7 (m, 12 H), 0.82 (s, 3 H), 3.85 (m, 4 H), 4.18 (m, 1 H), 4.53 (m, 1 H), and 4.88 ppm (m, 1 H). *Anal.* Calcd for $C_{14}H_{22}O$: C, 70.55; H, 9.31. Found: C, 70.73; H, 9.04.

Keto-Allylic Ester 8. To 1.26 g (5.30 mmol) of ketal-alcohol allylic alcohol **7** in 10 ml of dry pyridine was carefully added 0.80 g (6.63 mmol) of pivalyl chloride. The mixture was stirred for 20 hr at room temperature, and water was added. The solution was thoroughly extracted with ether, and the combined extracts were washed with cold 6 *N* hydrochloric acid, water, cold 3 *N* sodium hydroxide, water, and saturated sodium chloride solution. After drying, the solvent was removed, and the crude product was used without further purification: nmr (CCl_4) δ 0.6–2.5 (m, 11 H), 0.82 (s, 3 H), 1.14 (s, 9 H), 3.82 (m, 4 H), 4.67 (m, 1 H), 5.04 (m, 1 H), and 5.27 ppm (m, 1 H).

The ketal from the above reaction was dissolved in 50 ml of acetone, and 100 mg of *p*-toluenesulfonic acid was added. The mix-

ture was stirred for 14 hr. After the addition of 1 g of solid potassium carbonate, the solution was stirred for 1 hr. Filtration removed the solid material, and the acetone was evaporated at reduced pressure. Ether was added to the residue, and the solution was washed with 5% sodium hydroxide, water, and saturated sodium chloride solution and was dried. The solvent was removed, and the crude product was chromatographed on Florisil to yield 1.25 g [86% based on alcohol **7**] of keto-allylic ester **8**; ir (neat) 1645 (C=C) and 1720 cm^{-1} (C=O); nmr (CCl_4) δ 0.6–2.8 (m, 11 H), 0.70 (s, 3 H), 1.19 (s, 9 H), 4.80 (m, 1 H), 5.19 (m, 1 H), and 5.36 ppm (m, 1 H); high resolution mass spectrum, *m/e* 278.1896 (calcd for $C_{17}H_{26}O_3$, 278.1882).

Keto-Diester 9. To 1.85 g (6.31 mmol) of keto-allylic ester **8** in 75 ml of dry benzene were added 0.79 ml (9.45 mmol) of pyrrolidine and ~10 mg of *p*-toluenesulfonic acid. The flask was fitted with a Dean-Stark trap, and the mixture was refluxed for 25 hr. The trap was replaced by a reflux condenser, and 5.00 g (19.0 mmol) of methyl bromoacetate was added dropwise to the refluxing solution. The mixture was refluxed for an additional 24 hr. After the mixture was cooled to room temperature, 25 ml of an aqueous sodium acetate–acetic acid–water (1:2:2) buffer was added, and the solution was refluxed for 6 hr. Ether was added, and the aqueous phase was separated. The extract was washed with 3 *N* sodium hydroxide until basic, followed by water and saturated sodium chloride solution, then dried, and concentrated. The crude reaction product was chromatographed on Florisil to give 1.41 g (64%) of keto-diester **9**: ir (CCl_4) 1640 (C=C), 1710 (C=O), and 1740 cm^{-1} (O–C=O); nmr ($CDCl_3$) δ 0.70 (s, 3 H), 1.24 (s, 9 H), 0.7–3.2 (m, 12 H), 3.73 (s, 3 H), 4.82 (m, 1 H), 5.24 (m, 1 H), and 5.44 ppm (m, 1 H); high resolution mass spectrum, *m/e* 350.2078 (calcd for $C_{20}H_{30}O_5$, 350.2093).

Lactone-Ester 10. To 922 mg (2.64 mmol) of keto-diester **9** in 10 ml of methanol cooled to 0° was added 100 mg (2.64 mmol) of sodium borohydride. The mixture was stirred for 12 hr as the bath gradually warmed to room temperature. The reaction mixture was washed into a separatory funnel with a large excess of ether, and 5 ml of 10% hydrochloric acid was added. After shaking for 5 min, the aqueous layer was discarded, and the organic layer was washed with saturated sodium chloride solution until neutral. The extract was dried and concentrated. Column chromatography of the crude product on Florisil yielded 640 mg (76%) of crystalline lactone-ester **10**. An analytical sample was recrystallized from ether: mp 114–115°; ir (CCl_4) 910 (O=CH_2), 1648 (C=C), 1730 (C=O), and 1790 (O–C=O); nmr (CCl_4) δ 0.7–2.3 (m, 12 H), 0.84 (s, 3 H), 1.13 (s, 9 H), 4.52 (m, 1 H), 4.75 (m, 1 H), 5.12 (m, 1 H), and 5.28 ppm (m, 1 H). *Anal.* Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.47; H, 8.87.

Lactone-Diester 11. To 105 mg (2.50 mmol) of sodium hydride (57% oil dispersion, washed three times with petroleum ether) were added 10 ml of dry dimethyl carbonate and 400 mg (1.25 mmol) of lactone-ester **10**. The mixture was refluxed for 14 hr, and water was added. The solution was thoroughly extracted with ether, and the combined extracts were washed with 5% hydrochloric acid, water, and saturated sodium chloride solution and dried. The solvent was removed to yield 435 mg (98%) of lactone-diester **11** as a white solid that was used in the following reaction without further purification. An analytical sample was recrystallized from methanol: mp 152–153°; ir (CH_2Cl_2) 1645 (C=C), 1735 (C=O) and 1770 cm^{-1} (O–C=O); nmr ($CDCl_3$) 0.8–3.0 (m, 10 H), 0.82 (s, 3 H), 3.36 (s, 1 H), 3.78 (s, 6 H), 4.80 (m, 1 H), 4.88 (m, 1 H), and 5.20 ppm (m, 2 H). *Anal.* Calcd for $C_{18}H_{24}O_7$: C, 61.35; H, 6.86. Found: C, 61.46; H, 6.99.

Hydroxy-Lactone-Ester 12. To 335 mg (0.95 mmol) of lactone-diester **11** were added 5 ml of methanol, 1 ml of water, and 224 mg (4 mmol) of potassium hydroxide. After heating for 5 hr at 50°, the mixture was cooled to 0°, acidified with 6 *N* hydrochloric acid, and thoroughly extracted with ether. The combined extracts were washed with water and saturated sodium chloride solution and dried. The solvent was removed, and the residue was taken up in ether. Diazomethane was added until a yellow color persisted, and nitrogen ceased to be evolved. The ether was evaporated and the residue was washed into a separatory funnel with additional ether. Cold 6 *N* hydrochloric acid was added, and the mixture was shaken for 5 min. The organic layer was washed with water and saturated sodium chloride solution and dried. The solvent was removed, and the crude product was chromatographed on Florisil to give 171 mg (61%) of crystalline hydroxy-lactone-ester **12**. An analytical sample was recrystallized from ether: mp 134–136°; ir ($CHCl_3$) 1638 (C=C), 1725 (C=O), 1775 (O–C=O), and 3610 cm^{-1} (OH); nmr ($CDCl_3$) δ 0.6–2.4 (m, 11 H), 0.82 (s, 3 H), 3.33 (s, 1 H), 3.77 (s, 3 H), 4.34 (m, 1 H), 4.60 (m, 1 H), 4.84 (broad, 1 H), and 4.95 ppm (s, 1 H). *Anal.* Calcd for $C_{16}H_{18}O_5$: C, 65.29; H, 7.53. Found: C, 65.25; H, 7.59.

(±)-Isotelekin (1). To 2.0 ml (30.0 mmol) of dimethylamine in 4 ml of dioxane were added 50 mg (0.612 mmol) of dimethylamine hydrochloride and 0.2 ml (0.024 mmol) of 37% aqueous formaldehyde. The mixture was stirred for 30 min, and 53 mg (0.18 mmol) of hydroxy-lactone-ester **12** was added. After the mixture was stirred for 10 hr at room temperature, ether was added. The organic layer was washed with 6 *N* sodium hydroxide, water, and saturated sodium chloride solution and dried. The solvent was removed to yield 59 mg of the crude Mannich base.

The crude product from above was dissolved in 1 ml of methyl iodide, and the mixture was stirred for 10 hr at room temperature. Excess methyl iodide was removed, and the solid was triturated with ether to yield 32 mg of crystalline quaternary ammonium salt. Evaporation of the ether washes yielded 26 mg of unreacted hydroxy-lactone-ester **12**.

To 32 mg of the quaternary salt was added 2 ml of dimethylformamide, and the mixture was heated at 80° for 18 hr. Ether was added to the cooled solution, and the organic layer was washed with water and saturated sodium chloride solution and dried. The solvent was removed, and the crude product was chromatographed on Florisil to yield 18 mg (86% based on recovered **12**) of synthetic isotelekin. A sample was recrystallized from an ether–petroleum ether mixture, mp 159–160°. The synthetic material was found to have identical solution infrared and nuclear magnetic resonance spectra with an authentic sample of natural isotelekin: ir ($CHCl_3$) 910 (s), 948 (s), 965 (w), 990 (w), 1010 (w), 1035 (s), 1055 (w), 1130 (m), 1155 (s), 1220 (s), 1303 (w), 1340 (w), 1380 (w), 1420 (w), 1645 (w), 1660 (w), 1755 (s), 2950 (s), 3005 (m), 3090 (w), 3500 (m), and 3610 (m) cm^{-1}; nmr ($CDCl_3$) δ 0.7–3.0 (m, 11 H), 0.79 (s, 3 H), 4.30 (m, 1 H), 4.48 (m, 1 H), 4.56 (m, 1 H), 4.97 (m, 1 H), 5.57 (m, 1 H), and 6.10 ppm (m, 1 H).

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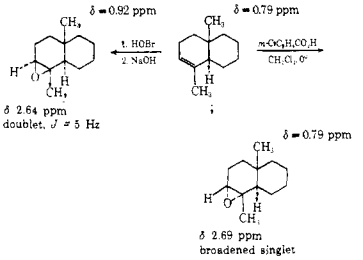

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Communications to the Editor

^{13}C Nuclear Magnetic Resonance of $[Rh_6(CO)_{15}C]^{2-}$

Sir:

The carbide atom in transition metal carbonyl cluster carbides has been claimed to result from two different sources: bonded carbon monoxide is believed to disproportionate to carbon and carbon dioxide,[1] and, recently, halocarbons such as $CHCl_3$[2] and CCl_4 have been found to be the source of the carbide atom, according to the reactions

$$6[RhCl_6]^{3-} + 23OH^- + 26CO + CHCl_3 \xrightarrow[25°,\,1atm]{MeOH} [Rh_6(CO)_{15}C]^{2-} + 39Cl^- + 11CO_2 + 12H_2O \quad (1)$$

(yield ~80%)

$$6[NMe_3Bz][Rh(CO)_4] + CCl_4 \xrightarrow[25°]{i\text{-}PrOH} [NMe_3Bz]_2[Rh_6(CO)_{15}C] + 4[NMe_3Bz]Cl + 9CO \quad (2)$$

(yield ~90%)

Although we have observed that in both cases the carbide cluster is not obtained in the absence of the halocarbon, in view of the novelty of these syntheses we wished to have unequivocal proof of the source of the carbide atom in the $[Rh_6(CO)_{15}C]^{2-}$ dianion. To this end we have synthesized $[Rh_6(CO)_{15}{}^{13}C]^{2-}$ (*ca.* 90% ^{13}C) starting from $^{13}CCl_4$ and the $[Rh(CO)_4]^-$ anion, and the ^{13}C nmr spectrum of this species has been recorded in perdeuterioacetone solution containing $Cr(acac)_3$ as relaxing agent.[3] The resonance of the carbide carbon should show a septet pattern due to coupling with six equivalent rhodium atoms. Both at room temperature and at −70°, the spectrum (Figure 1a) shows a symmetrical five-line pattern and it seems probable that the outer lines of the expected septet are not resolved since the relative intensities of the five lines, 8.6:15.7:20.0:15.2:8.4, show better agreement with the relative intensities of a septet rather than a quintet pattern. The spacing between the lines is 13.7 ± 2 Hz and this low value of $^1J(Rh\text{-}C_D)$ (see Figure 2) is consistent with the expected low s character of the rhodium–carbide bonds. The carbide resonance (264.7 ppm)[4] occurs at very low field and is in the region found for carbonium ions[5] and rhodium carbene complexes.[6] The shortness of the carbide radii in similar clusters of ruthenium[7] and iron[8] is in favor of a positive and contracted carbide atom.

^{13}CO interexchange with $[Rh_6(CO)_{15}C]^{2-}$ occurs very slowly at room temperature and atmospheric pressure. At 80° (in tetrahydrofuran solution) exchange is faster, but decomposition to give uncharacterised species also takes place. However, under these last conditions we were able to

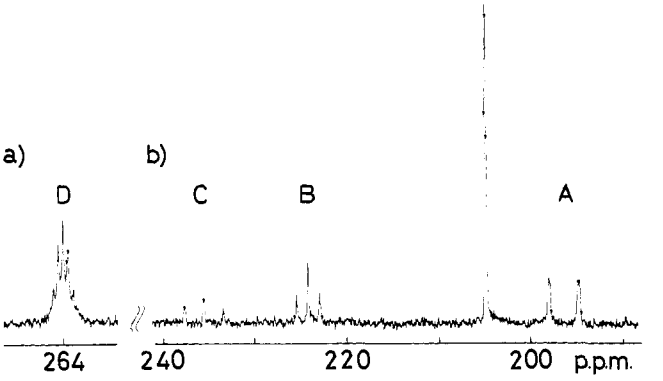

Figure 1. The ^{13}C nmr spectrum of (a) $[Rh_6(CO)_{15}{}^{13}C]^{2-}$ (*ca.* 90% ^{13}C) and (b) $[Rh_6(CO)_{15}C]^{2-}$ (*ca.* 42% ^{13}CO) at −70° in perdeuterioacetone solution in the presence of $Cr(acac)_3$.

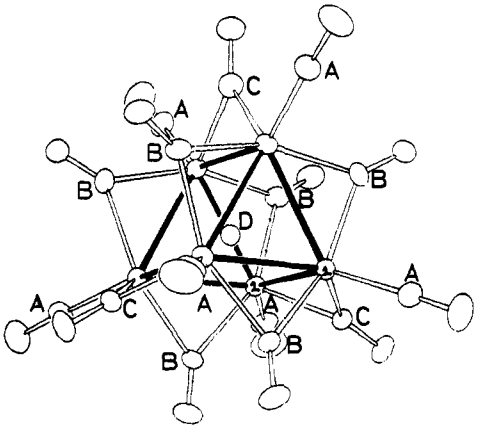

Figure 2. The X-ray structure of $[Rh_6(CO)_{15}C]^{2-}$.[2]