showed that two products had been formed in a 5:1 ratio. The isomers were separated by preparative vpc (12 ft × 0.25 in., 10% Carbowax 6000 on Chromosorb G, 160°).

The major isomer had the longest vpc retention time: ν_{max}^{neat} 2850, 2800, 2660, 1470, 1450, 1345, and 1000 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 1.22 and 1.53 (centers of two broad overlapping singlets, high field signal has greater height).

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.75; H, 13.34.

The minor isomer had the shortest retention time: ν_{max}^{neat} 2850, 2800, 2660, 1480, 1460, 1445, and 1355 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 1.19 and 1.59 (centers of two broad overlapping singlets, low field signal has greatest height).

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.74; H, 13.22.

B. Reduction of Benzocyclooctene. A solution of 1.56 g (9.65 mmol) of benzocyclooctene in 100 ml of glacial acetic acid was hydrogenated for 72 hr over 250 mg of 5% rhodium on alumina at 60° under 50 psi hydrogen in a Paar hydrogenation apparatus. The solution was diluted with water (600 ml) and extracted with pentane (3 × 250 ml). The extracts were washed with water, dried, and evaporated through a metal helix-packed column. Analysis of the clear residue by vpc showed two products were present in a 5:1 ratio. The isomers were separated by preparative vpc (12 ft × 0.25 in., 10% Carbowax 6000 on Chromosorb G, 160°) and were identical in every respect with those obtained above.

Pyrolysis of 38a. A 120 mg (0.540 mmol) sample of **38a** was passed through a quartz chip packed quartz tube heated at 400° at 10 mm with a slow stream of nitrogen. There was obtained 78.3 mg (91.5%) of tetraene **27** as a yellow oil. An analytical sample of the yellow liquid obtained by preparative vpc was identical in all respects with that isolated above.

Photolysis of 38a. A solution of 10.7 mg (0.048 mmol) of **38a** in 3 ml of acetone was irradiated with a 200-W Hanovia lamp equipped with Corex optics. Monitoring of the photolysis by tlc showed no sulfone remained after 30 min. Preparative vpc (5 ft × 0.25 in., 5% Carbowax 20M on Chromosorb G, 130°) was used to isolate the sole volatile component. It was spectrally identical with authentic **27**.

2,3,4,5,6,11-Hexahydro-6,11-epithio-1*H*-cycloheptacyclooctene 12,12-Dioxide (38b). To a magnetically stirred solution of 666 mg (2.44 mmol) of α-chloro sulfone **37b**[23] in 75 ml of dry dimethyl sulfoxide under nitrogen was added 863 mg (7.70 mmol) of potassium *tert*-butoxide, and the dark green solution was stirred for 15 min. With cooling, 25 ml of ice–water was added and the solution was extracted three times with ether. The combined extracts were washed, and dried, and the solvent was removed to afford 322 mg (55.8%) of **38b**: mp 149.5–150.5°, from ether–methylene chloride; $\nu_{max}^{CHCl_3}$ 1310, 1130, and 1110 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.90–6.10 (m, 4, olefinic), 3.73–3.97 (m, 2, >CHSO$_2$–), 2.22–2.58 (m, 4, allyl), and 1.35–1.95 (m, 6, methylene).

Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.08; H, 6.83; S, 13.55. Found: C, 66.06; H, 6.94; S, 13.32.

Bicyclo[6.5.0]trideca-1,3,5,7-tetraene (39). A solution of 87.0 mg (0.368 mmol) of **38b** in acetone was irradiated with a 450-W Hanovia lamp through a Corex filter for 60 min. By preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 130°) there was isolated 23.0 mg (37%) of **39** as a yellow oil: ν_{max}^{neat} 2960, 2890, 2820, 1450, and 690 cm^{-1}; $\lambda_{max}^{isooctane}$ 285 sh nm (ε 123); $\delta_{TMS}^{CDCl_3}$ 5.53–5.90 (m with sharp singlet at 5.75, 6, olefinic), 2.0–2.5 (m, 4, allyl), and 1.57 (br s, 6, methylene).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.60; H, 9.52.

5,10-Dihydro-5,10-epithiobenzocyclooctene 11,11-Dioxide (43). To a magnetically stirred solution of 234 mg (0.931 mmol) of α-chloro sulfone **42**[23] in 30 ml of dry dimethyl sulfoxide under nitrogen was added 112 mg (1.00 mmol) of potassium *tert*-butoxide, and the deep green solution was stirred for 30 min. With cooling, 50 ml of water was added and the solution was acidified with concentrated hydrochloric acid. The aqueous solution was extracted with chloroform and the extract was washed with water and brine and dried. Evaporation of the solvent and recrystallization from methanol–chloroform gave 137 mg (68.4%) of **43** as a white crystalline solid: mp 269.0–271.0° dec, from ether–chloroform; ν_{max}^{KBr} 1310, 1190, and 1100 cm^{-1}; $\delta_{TMS}^{DMSO\text{-}d_6}$ 7.43 (s, 4, aromatic), 5.93 (br s, 4, olefinic), and 4.90–5.07 (m, 2, >CHSO$_2$–); $\lambda_{max}^{C_2H_5OH}$ 267 sh (ε 2280), 273 (2470), and 278 sh (2280).

Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.05; H, 4.62; S, 14.66. Found: C, 65.77; H, 4.61; S, 14.82.

Benzocyclooctatetraene (44) from 43. A solution of 25.0 mg (0.116 mmol) of **43** in acetone was irradiated for 3 hr with a 200-W Hanovia lamp equipped with a Vycor filter. Analysis of the photolysis solution showed only one volatile component. Preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 120°) gave 16.2 mg (91%) of crystalline benzocyclooctatetraene (**44**), mp 49–50°, identical upon spectral comparison with an authentic sample.[48]

(48) L. B. Anderson and L. A. Paquette, *J. Amer. Chem. Soc.*, **94**, 4915 (1972); L. Friedman and D. F. Lindow, *ibid.*, **90**, 2329 (1968).

Olefin Isomerizations Accompanying the Hydroformylation of 3-Methyl-1-hexene-*3*-d_1[1]

Charles P. Casey* and Clifford R. Cyr

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received August 7, 1972*

Abstract: The dicobalt octacarbonyl catalyzed hydroformylation of 3-methyl-1-hexene-*3*-d_1 (**1**-*d*) followed by oxidation and esterification gives 3.1% methyl 3-(ethyl-*1*-d_1)hexanoate (**3**-*d*) in addition to the normal hydroformylation products. The Eu(DPM)$_3$-shifted nmr spectra of **3**-*d* demonstrated that a 1,2 migration of deuterium had occurred in the hydroformylation of **1**-*d*. This result taken together with Pino's observation that the hydroformylation of optically active **1** gives **3** with 70% retention of optical activity demonstrates that **3**-*d* is formed by multiple isomerizations of the complexed alkene which immediately precede hydroformylation. The rate of isomerization of the complexed alkene consequently must be greater than the rate of decomplexation. A mechanism, previously proposed by Pino, involving direct insertion of cobalt into a carbon–hydrogen bond of a methyl group, is directly refuted by the results obtained here.

Hydridotetracarbonylcobalt is the active catalyst in the dicobalt octacarbonyl catalyzed hydroformylation of olefins.[2] Depending on the reaction conditions employed, olefin isomerization accompanying hydro-

(1) Some of the results described in this paper have appeared in preliminary form: C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **93**, 1280 (1971).

(2) For reviews of hydroformylation, see (a) A. J. Chalk and J. F. Harrod, *Advan. Organometal. Chem.*, **6**, 119 (1968); (b) R. F. Heck, *ibid.*, **4**, 243 (1966); (c) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967, Chapter 6.

formylation may be either extensive[3] or minimal.[4] Hydridotetracarbonylcobalt is known to catalyze olefin isomerization; both a metal hydride addition–elimination mechanism[5] and a π-allyl metal hydride mechanism[6] have been proposed for the isomerization. Recently, Pino, *et al.*,[7] suggested that a third type of reaction, the insertion of cobalt into a carbon–hydrogen bond of a complexed alkene, can occur under hydroformylation conditions. They proposed that the small amount of (*R*)-3-ethylhexanal (**2**) formed in the hydroformylation of (+)-(*S*)-3-methyl-1-hexene (**1**) arises *via* insertion of cobalt into a carbon–hydrogen bond.

The hydroformylation (+)-(*S*)-3-methyl-1-hexene (**1**) gives 3.6% (*R*)-3-ethylhexanal (**2**) in addition to the normal hydroformylation products 4-methylheptanal (93.0%) and 2,3-dimethylhexanal (3.4%).[7] Since the hydroformylation was run under conditions which minimize olefin isomerization and since **2** was formed with >70% retention of configuration, a mechanism involving 2-ethyl-1-pentene as an intermediate was excluded.

Pino, *et al.*, proposed that **2** arose *via* direct insertion of cobalt into a carbon–hydrogen bond of the methyl group of **1** followed by hydroformylation.[7] The related insertions of transition metals into the ortho carbon–hydrogen bonds of arylphosphines, aryl phosphites, benzylamines, and azobenzenes[8] and into the methyl groups of methylphosphines[9] and *o*-tolylphosphines[10] are now well documented. However, the proposed insertion of cobalt into the methyl group of **1** would be very unusual; the methyl carbon–hydrogen bonds in **1** are unactivated by adjacent aromatic rings or phosphorus or nitrogen heteroatoms. Only two examples of the insertion of a metal into an unactivated alkyl–hydrogen bond have been reported.[11]

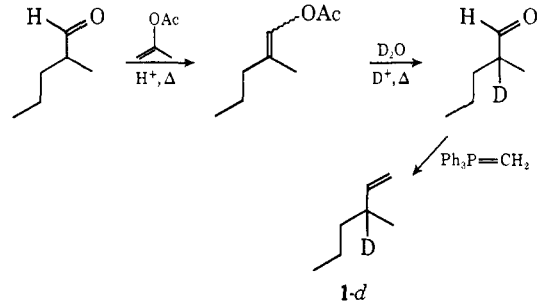
There are two alternate explanations for the retained stereochemistry of **2** which Pino did not consider. Retention could have resulted either from isomerization of an alkylcobalt intermediate by successive elimination and addition of cobalt hydride[12] or from isomerization of an intermediate cobalt–olefin complex *via* 1,3-hydrogen shifts.[13] In both cases, optical activity would be retained because of the asymmetry of the organocobalt intermediates.

To distinguish between these mechanisms, we have examined the hydroformylation of 3-methyl-1-hexene-*3-d*$_1$ (**1**-*d*). Direct insertion into the methyl group would leave the label unshifted, while isomerization *via* an addition–elimination process would lead to migration of deuterium to the methylene carbon of the ethyl group in **2** and isomerization *via* 1,3-hydrogen shifts in an olefin complex would lead to deuterium in the methyl group of the ethyl side chain of **2**.

Results

Synthesis. **1**-*d* was synthesized as shown in Scheme I by the Wittig reaction of 2-methylpentanal-*2-d*$_1$ (95% d_1) with methylenetriphenylphosphorane. When the Wittig reaction was run using dimsyl anion (from NaH) in dimethyl sulfoxide as the base to form methylenetriphenylphosphorane, the yield of **1**-*d* was 60–70%, but substantial amounts of benzene (30–40%), difficult to separate from **1**-*d*, were also produced and 20% loss of deuterium in **1**-*d* was observed. When *n*-butyllithium in a hexane–tetrahydrofuran mixture was used as the base to generate methylenetriphenylphosphorane, the yield of **1**-*d* was reduced to 20–40% but contamination by benzene was reduced to 5% and loss of deuterium was not as severe. Final purification by spinning band distillation and gas chromatography gave pure **1**-*d* (85% d_1).

Scheme I



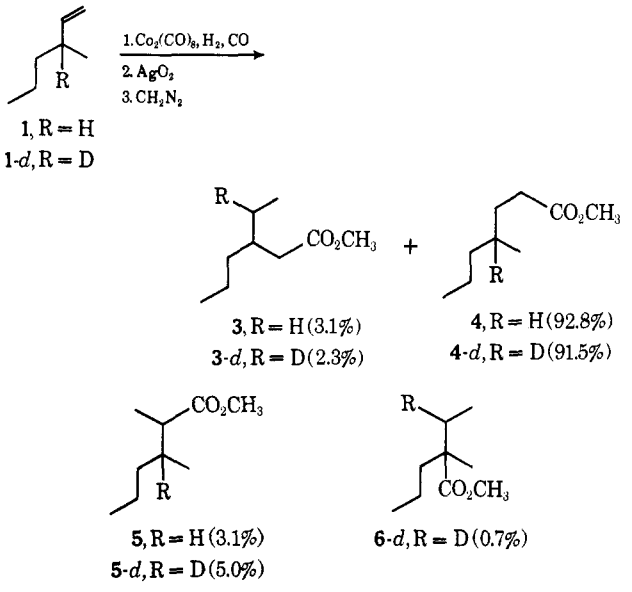
1-*d*

Hydroformylation. The hydroformylation of **1**-*d* was conducted under conditions similar to those used by Pino.[7] A solution of 3.0 g of **1**-*d* in 15 ml of benzene containing 64 mg of $Co_2(CO)_8$ was heated to 110° for 24 hr under 100 atm of H_2 and 100 atm of CO pressure in a glass-lined bomb. The reaction mixture was bulb-to-bulb distilled and the mixture of aldehydes was immediately oxidized with silver(I) oxide; the resulting acids were converted to the corresponding methyl esters by treatment with diazomethane in ether. Gas chromatographic analysis (10 ft × 0.25 in., 17% Carbowax 20M, Chromosorb P, 125°) showed that the mixture of esters consisted of 2.3% methyl 3-ethylhexanoate (**3**), 91.5% methyl 4-methylheptanoate (**4**), 5.0% methyl 2,3-dimethylhexanoate (**5**), 0.7% methyl 2-methyl-2-ethylpentanoate (**6**), and 0.5% of an unidentified methyl ester. Pure samples of **3**, **4**, and **5** were obtained by preparative gas chromatography and were identified by spectral comparison with authentic samples of undeuterated compounds prepared by unambiguous routes. **6** was identified by comparison of gas chromatographic retention time with that of an authentic sample.

Deuterium Labeling of Esters. The location of

(3) M. Johnson, *J. Chem. Soc.*, 4859 (1963).
(4) P. Pino, S. Pucci, and F. Piacenti, *Chem. Ind. (London)*, 294 (1963); F. Piacenti, P. Pino, R. Lazzaroni, and M. Bianchi, *J. Chem. Soc. C*, 488 (1966).
(5) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 4023 (1961).
(6) (a) L. Roos and M. Orchin, *ibid.*, **87**, 5502 (1965). (b) More recent studies by Orchin indicate that hydridotetracarbonylcobalt catalyzes olefin isomerization, at least in part, by the addition–elimination mechanism: P. Taylor and M. Orchin, *ibid.*, **93**, 6504 (1971). (c) See also R. Cramer and R. V. Lindsey, Jr., *ibid.*, **88**, 3534 (1966).
(7) F. Piacenti, S. Pucci, M. Bianchi, and P. Pino, *ibid.*, **90**, 6847 (1968).
(8) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970), and references therein.
(9) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).
(10) (a) M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, **91**, 6226 (1969); (b) R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970).
(11) (a) The insertion of platinum into an *n*-propyl group of *trans*-$PtCl_2[P(tert\text{-}Bu)_2(n\text{-}Pr)]_2$ was recently claimed: A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Commun.*, 1205 (1970); *J. Chem. Soc. A*, 3833 (1971). (b) An exchange reaction between the complex $HOsCl(CO)(Pcy_3)_2$ and deuterium during preparation of the complex has been suggested to explain the appreciable deuteration of the cyclohexyl phosphine ligands: F. G. Moers, *Chem. Commun.*, 79 (1971).
(12) A similar mechanism was advanced to account for the 2.9% 3-methylhexanal present in the hydroformylation mixture of 4-methyl-1-pentene when only 1% olefin isomerization was observed.[2a]
(13) See C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, submitted for publication, for a discussion of the π-allyl metal hydride mechanism for olefin isomerization which proceeds *via* 1,3 hydrogen shifts.

Scheme II



deuterium in methyl 3-ethylhexanoate (**3-*d***) (84% d_1 by mass spectrometry) was determined from its nmr spectrum in the presence of tris(dipivaloylmethanato)-europium(III), Eu(DPM)$_3$, a reagent which induces pseudocontact chemical shifts in molecules capable of coordination with europium[14] (see Figure 1). In the nmr spectrum of undeuterated **3** taken in the presence of 30 mol % Eu(DPM)$_3$, all absorptions but those due to two methylene groups are cleanly separated and first order; the tertiary hydrogen atom appears as a multiplet at δ 5.2 and the methyl protons of the ethyl group are a sharp triplet at 1.7. In a similar Eu(DPM)$_3$-shifted spectrum of the deuterated ester **3-*d***, the presence of a tertiary proton is clearly indicated by the multiplet at δ 5.2 and by the presence of a doublet at δ 6.3 for the protons adjacent to the carbonyl and coupled to the methine proton. The presence of a deuterium atom on the methylene carbon of the ethyl side chain is indicated by the collapse of the methyl triplet to a doublet at δ 1.7 and by a decrease in the integral for the broad multiplet at δ 3.1. Integration of the complex absorption between δ 3.6 and 2.0 indicated that **3-*d*** had only 5.17 $\pm$ 0.10 methylene protons compared with 6.0 in the undeuterated material. Integration of the multiplet at δ 5.2 indicated the presence of 1.1 $\pm$ 0.1 tertiary protons. Consequently, within experimental error, all of the deuterium in **3-*d*** has been shifted from the tertiary carbon to the methylene carbon of the ethyl side chain.

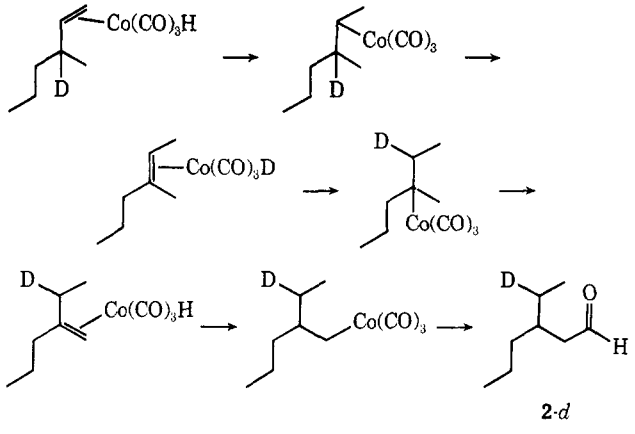
In similar fashion, the deuterium atom in the normal hydroformylation products methyl 4-methylheptanoate **4-*d*** and the diastereomeric mixture of methyl 2,3-dimethylhexanoate **5-*d*** was located from analysis of their Eu(DPM)$_3$-shifted nmr spectra. In the Eu(DPM)$_3$-shifted nmr spectrum of **4**, the tertiary hydrogen appears as a multiplet at δ 2.6 and the 4-methyl group appears as a doublet at 1.5; in a similar spectrum of the deuterated ester **4-*d***, the presence of a deuterium atom on the tertiary carbon atom is indicated by the absence of the tertiary hydrogen atom multiplet at δ 2.6 and the collapse of the 4-methyl doublet at 1.5 to a singlet (see Figure 2). In the Eu(DPM)$_3$-shifted nmr spectrum of the diastereomeric mixture **5**, the tertiary hydrogen atom at carbon three appears as a multiplet at δ 3.7 and the 3-methyl group appears as two doublets (one doublet for each diastereomer) at 1.9 and 2.1; in a similar spectrum of deuterated **5-*d***, the presence of a deuterium atom on tertiary carbon atom three is indicated by the absence of the tertiary hydrogen multiplet and the collapse of the 3-methyl doublets to two singlets (see Figure 3). Therefore, these products were formed without shift of deuterium.

(14) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970); *J. Amer. Chem. Soc.*, **93**, 641 (1971).

Discussion

The formation of 3-(ethyl-*1*-d_1)hexanal (**2-*d***) in the hydroformylation of **1-*d*** establishes that a 1,2 deuterium shift accompanies the formation of this product. This result is best explained by an isomerization of a cobalt hydride complex of **1-*d*** proceeded by a series of cobalt hydride additions and eliminations which result in isomerization to a cobalt complex of 2-ethyl-1-pentene with an overall 1,2 deuterium migration (Scheme III).

Scheme III



To explain the retention of >70% optical activity in the formation of 3-ethylhexanal from optically active **1**, the hydroformylation of the complexed isomerized alkene must occur much more rapidly than decomplexation of the alkene.

The mechanism for the formation of **2** proposed by Pino is inconsistent with our results since it would have led to no deuterium shift in the course of the hydroformylation. Similarly, preisomerizations of a complexed alkene by a π-allyl metal hydride mechanism is eliminated since this would have led to a net 1,3 deuterium shift rather than the observed 1,2 shift. A π-allyl metal hydride mechanism for the isomerization of allylbenzene to β-methylstyrene catalyzed by HCo(CO)$_4$ has been proposed by Orchin.[6] However, his data are also consistent with a metal hydride addition–elimination mechanism.[6c]

The small amounts of isomeric hydroformylation products found here and the more rapid isomerization of the complexed alkene compared with the decomplexation of the alkene are in marked contrast with the results of Johnson[3] who found that olefin isomerization occurred rapidly in the hydroformylation of *neat* alkenes. Piacenti[4] has suggested that isomerization and exchange proceed *via* a HCo(CO)$_3$(alkene) species which has a significant lifetime under the conditions of Johnson's experiments, where the rapid hydroformylation rates in neat alkene mixtures create a local deficiency of carbon monoxide. In Piacenti's work, dilute benzene solutions of the alkene did not become carbon monox-

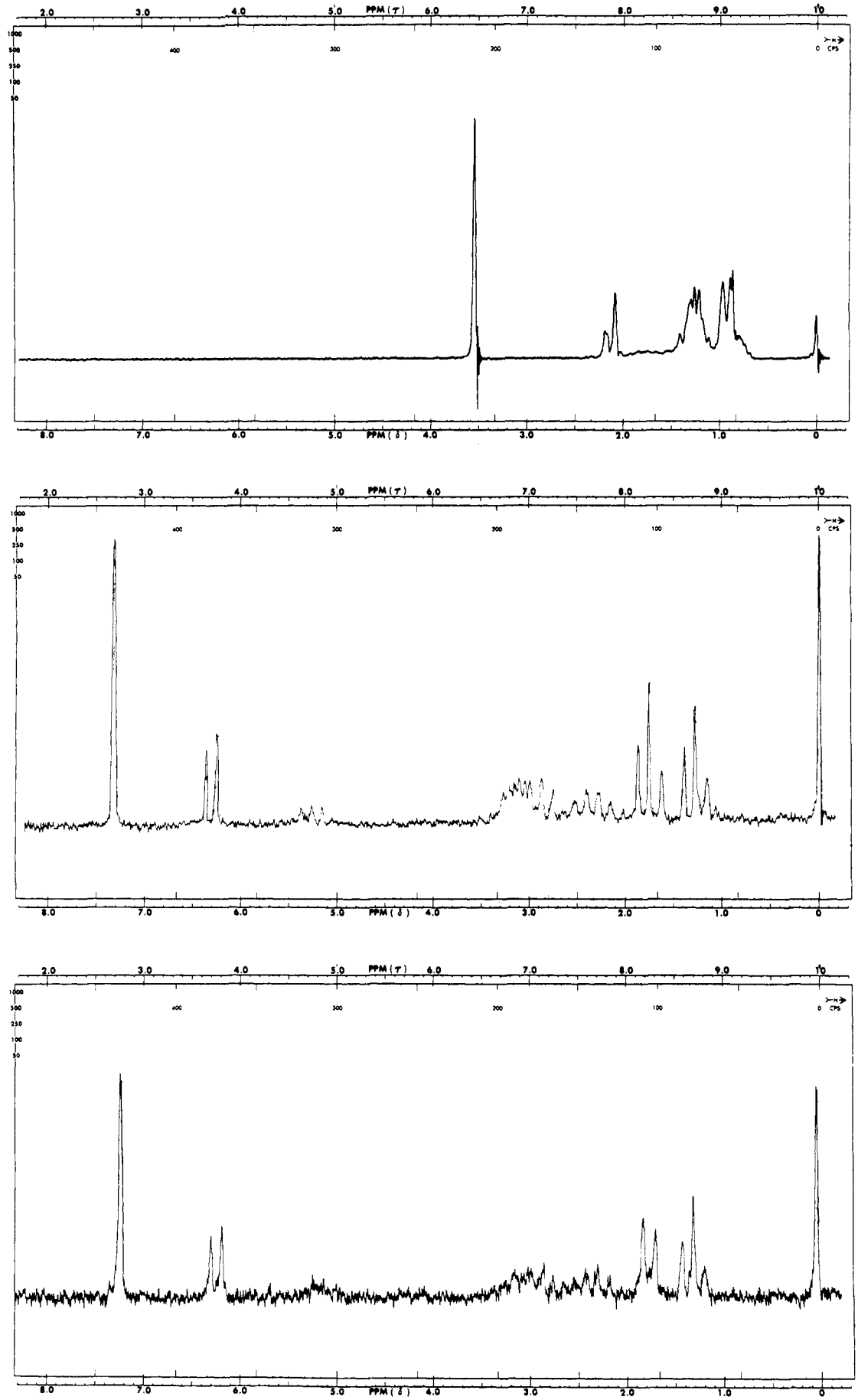


Figure 1. Nmr spectra at 60 MHz of methyl 3-ethylhexanoate in CCl_4: (top) normal spectrum of undeuterated ester; (center) spectrum of undeuterated ester in the presence of 30 mol % $Eu(DPM)_3$; (bottom) spectrum of deuterated ester in the presence of 30 mol % $Eu(DPM)_3$.

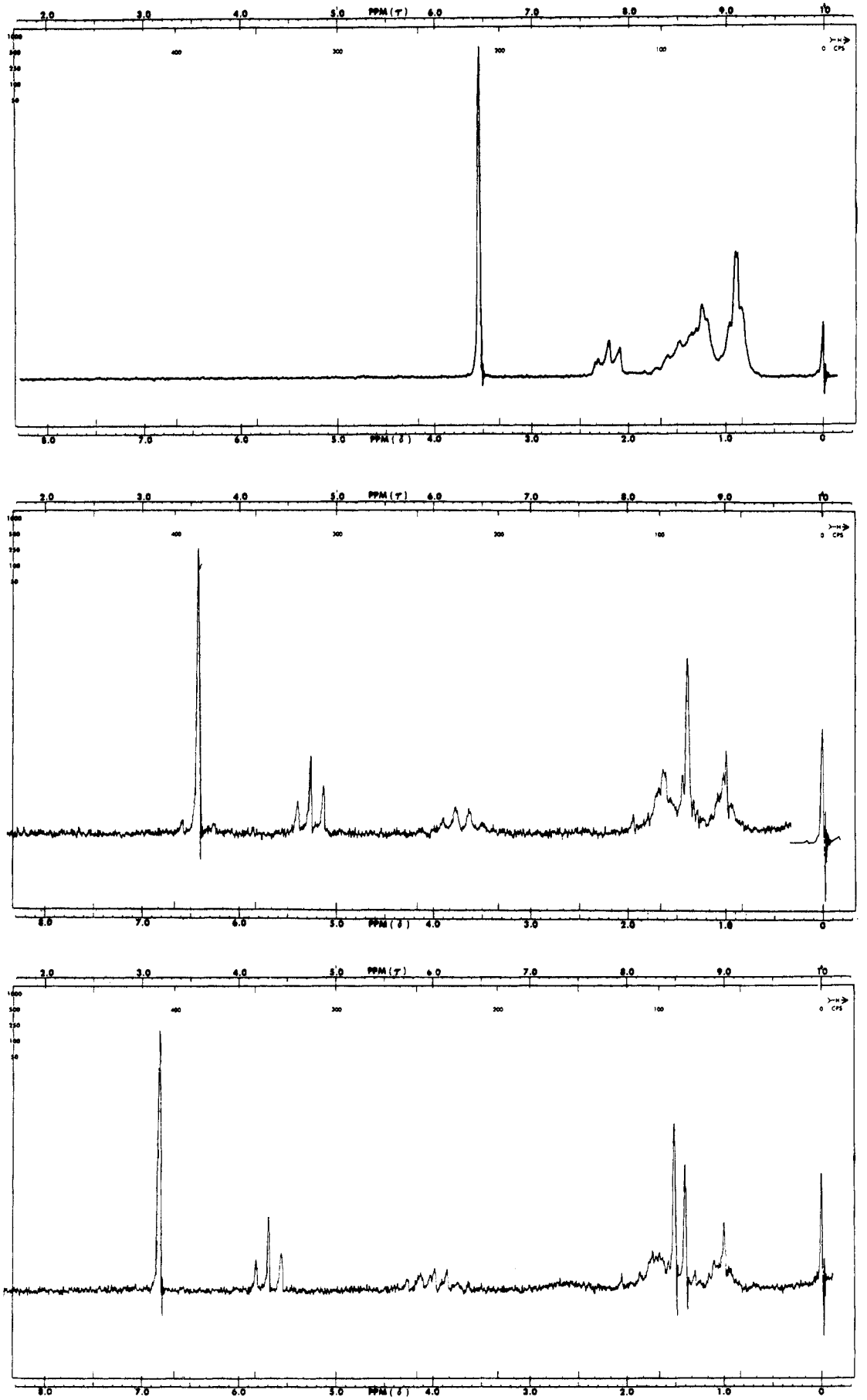


Figure 2. Nmr spectra at 60 MHz of methyl 4-methylheptanoate in CCl_4: (top) normal spectrum of undeuterated ester; (center) spectrum of undeuterated ester in the presence of 30 mol % $Eu(DPM)_3$; (bottom) spectrum of deuterated ester in the presence of 40 mol % $Eu(DPM)_3$.

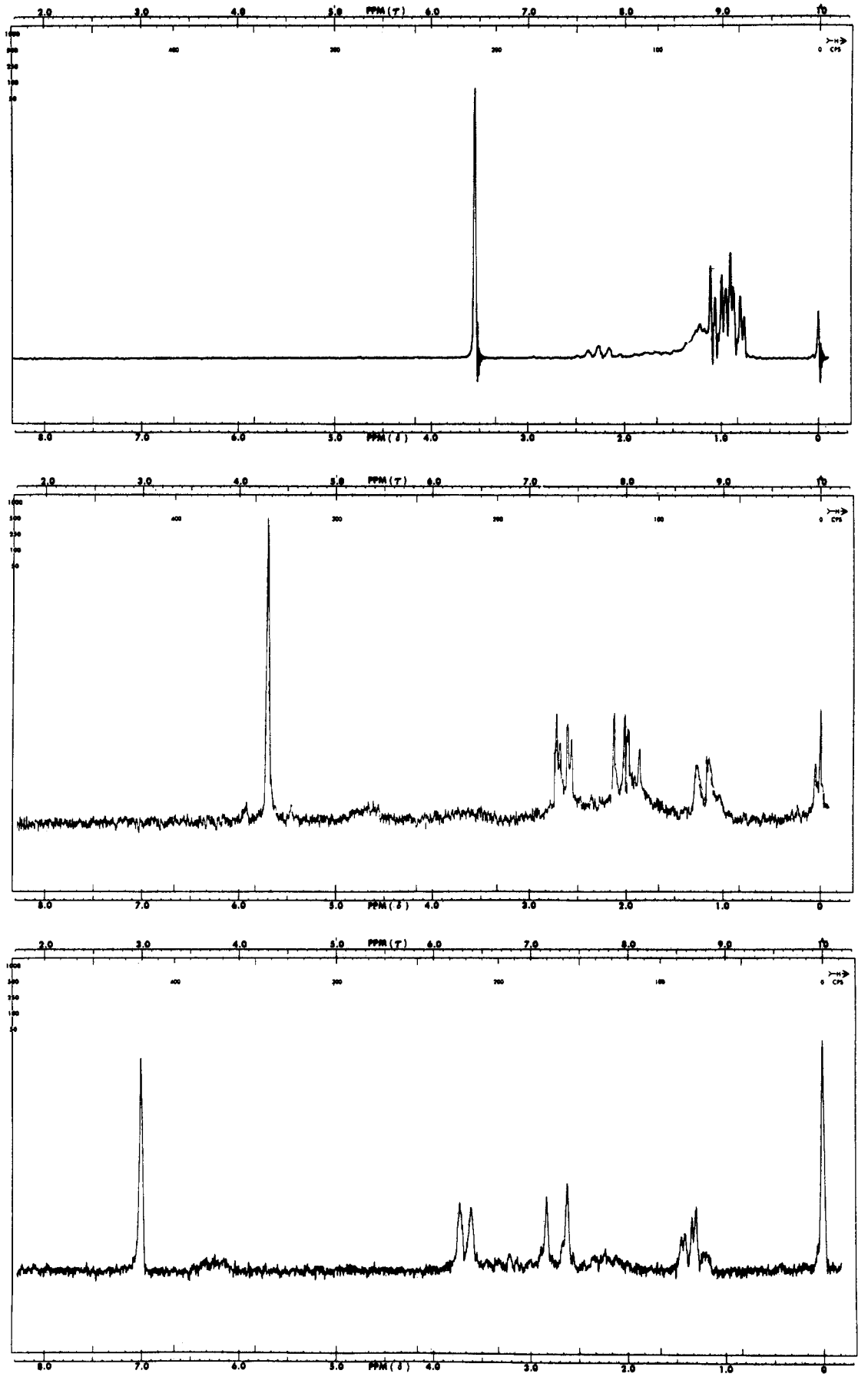


Figure 3. Nmr spectra at 60 MHz of methyl 2,3-dimethylhexanoate in CCl_4: (top) normal spectrum of undeuterated ester; (center) spectrum of undeuterated ester in the presence of 30 mol % $Eu(DPM)_3$; (bottom) spectrum of deuterated ester in the presence of 30 mol % $Eu(DPM)_3$.

ide starved and were found to hydroformylate without accompanying olefin isomerization. These results are best explained by a mechanism (see Scheme IV) similar

Scheme IV. Mechanism of Olefin Isomerization and Hydroformylation

$$HCO(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \quad (1)$$

$$HCo(CO)_3 + \text{alkene} \rightleftharpoons HCo(CO)_3(\text{alkene}) \quad (2)$$

$$HCo(CO)_3(\text{alkene}) + \text{alkene}' \rightleftharpoons HCo(CO)_3(\text{alkene}') + \text{alkene} \quad (3)$$

$$HCo(CO)_3(\text{alkene}) \rightleftharpoons RCo(CO)_3 \quad (4)$$

$$RCo(CO)_3 \rightleftharpoons HCo(CO)_3(\text{alkene}') \quad (5)$$

$$RCo(CO)_3 + CO \rightleftharpoons RCo(CO)_4 \quad (6)$$

$$RCo(CO)_4 \rightleftharpoons R{-}\overset{O}{\overset{\|}{C}}{-}Co(CO)_3 \quad (7)$$

$$R{-}\overset{O}{\overset{\|}{C}}{-}Co(CO)_3 + CO \rightleftharpoons R{-}\overset{O}{\overset{\|}{C}}{-}Co(CO)_4 \quad (8)$$

$$R{-}\overset{O}{\overset{\|}{C}}{-}Co(CO)_3 \xrightarrow{H_2} R{-}\overset{O}{\overset{\|}{C}}{-}H \quad (9)$$

to that of Breslow and Heck[5] in which $HCo(CO)_3$(alkene) either undergoes rapid alkene isomerization (eq 4 and 5) and alkene exchange (eq 3) or reacts with CO to give an $RCo(CO)_4$ species (eq 6) and eventually aldehyde. Consequently at high CO pressure there is little isomerization of olefins and exchange of alkenes on $HCo(CO)_3$(alkene). The isomerization of a complexed alkene is somewhat faster than the decomplexation of the alkene as demonstrated by the formation of 3-ethylhexanal with >70% retention of optical activity.

It is well known that high CO pressure inhibits hydroformylation as well as olefin isomerization. The isomerization, however, is inhibited more strongly than the hydroformylation as shown by the fact that isomeric products may be greatly decreased by operating at high CO and H_2 pressure.[4] A mechanism in which $HCo(CO)_3$(alkene) undergoes isomerization and $RCo(CO)_4$ undergoes hydroformylation readily explains why high CO pressure retards isomerization more than hydroformylation. The decreased rates of both isomerization and hydroformylation at high CO pressure can be explained by shifting equilibrium 1 from the catalytically active $HCo(CO)_3$ species and/or by shifting equilibrium 8 from the $RCOCo(CO)_3$ species active in hydroformylation toward the unreactive $RCOCo(CO)_4$ intermediate.

The multiple isomerization of a complexed alkene preceding hydroformylation is not unique. Multiple isomerizations *via* a metal hydride addition–elimination mechanism have also been suggested to explain the isomerization of an initial isopropyliridium compound to an *n*-propyliridium compound.[15] We have recently observed iron carbonyl catalyzed multiple olefin isomerizations of 3-ethyl-1-pentene which proceed *via* a π-allyl metal hydride mechanism.[13]

Experimental Section

Nmr spectra were recorded on Varian A-60A, T-60, and XL-100 spectrometers. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Mass spectra were determined on an AE1-902 mass spectrometer. A Hewlett-Packard Model 5750 research chromatograph was used for gas chromatographic analysis, and a Varian 90-P gas chromatograph was used for preparative gas chromatographic separations. Dicobalt octacarbonyl was prepared according to the method of Wender, *et al.*[16]

1-Acetoxy-2-methyl-1-pentene. Following analogous procedures of House,[17] isopropenyl acetate (710 g, 7.1 mol), 2-methylpentanal (360 g, 3.6 mol), and *p*-toluenesulfonic acid (2 g) were heated under nitrogen for 70 hr. Acetone was removed periodically by distillation through a 30-in. column filled with glass helices. The enol acetate was isolated from the reaction mixture by distillation under reduced pressure. Redistillation gave 345 g (67%) of 1-acetoxy-2-methyl-1-pentene (mixture of cis and trans isomers): bp 98–115° (107 mm); ir ν_{max}^{neat} 1740 (s), 1670 (w) cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.70–1.08 (t, 3 H, CH_3CH_2), 1.13–1.60 (m, 2 H, $CH_3CH_2CH_2$), 1.63 (s, 3 H, $CH_3C{=}C$), 1.7–2.2 (m, 2 H, $CH_2CH_2(CH_3)C{=}C$), 2.06 and 2.17 (s, 3 H, $CH_3CO_2C{=}C$; cis and trans isomers), and 6.83–7.0 (m, 1 H, $C{=}C(OAc)H$).

2-Methylpentanal-2-d_1. Following a procedure developed by Hine,[18] deuterium oxide (58.3 g, 2.92 mol), 1-acetoxy-2-methyl-1-pentene (344 g, 2.43 mol), and 3 drops of concentrated sulfuric acid were refluxed under nitrogen for 3 days. Ether (500 ml) was added to the cooled reaction mixture. The ether layer was washed successively with saturated Na_2CO_3 solution, saturated $NaHCO_3$ solution, and saturated NaCl solution, dried ($MgSO_4$), and distilled under nitrogen to give 200 g (80%) of 2-methylpentanal-2-d_1: bp 115–117°; ir ν_{max}^{neat} 2700 (m), 2110 (w), 1725 (s) cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.7–1.9 (m, 7 H, CH_3 and 2 CH_2), 1.08 (d, J = 1 Hz, 3 H, $CH_3CD(CH_3)$), and 9.44 (s, 1 H, CHO); 95% d_1.

3-Methyl-1-hexene-3-d_1. Butyllithium in hexane (0.90 mol) was added dropwise over 3 hr to a suspension of methyltriphenylphosphonium bromide (314 g, 0.88 mol) in 800 ml of dry THF maintained at −20 to −24°. The mixture was stirred under nitrogen for 12 hr at −24° and 1 hr at 10°. 2-Methylpentanal-2-d_1 (80 g, 0.80 mol) in 100 ml of dry THF was added over 7 hr at −24°. The mixture was then stirred for 16 hr at room temperature. Distillation under reduced pressure, water extraction of the THF, drying ($MgSO_4$), and spinning band distillation gave 13.7 g (18%) of 3-methyl-1-hexene-3-d_1; 88% d_1; ir ν_{max}^{neat} 2100, 1640, 990, and 910 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.65–1.10 (m, 6 H, 2 CH_3), 1.10–1.55 (m, 4 H, 2 CH_2), 4.63–5.13 (m, 2 H, $CH{=}CH_2$), and 5.32–6.02 (m, 1 H, $CDCH{=}CH_2$).

Hydroformylation of 3-Methyl-1-hexene-3-d_1. 3-Methyl-1-hexene-3-d_1 (3.0 g, 0.0305 mol) and dicobalt octacarbonyl (0.064 g, 0.187 mol) in 15 ml of dry benzene were placed in a 250-ml, high-pressure autoclave fitted with a glass liner. After flushing the autoclave with 1000 psi of nitrogen, it was filled with 600 psi of carbon monoxide and heated to 110°. An equimolar mixture of CO and H_2 (3000 psi) was added, and the autoclave was shaken for 40 hr. The autoclave was cooled rapidly and the pressure released. The reaction mixture was bulb-to-bulb distilled under vacuum.

Oxidation of the Hydroformylation Mixture. Addition of 50 ml of NaOH solution (13.5 g, 0.37 mol) to the mixture of aldehydes and silver nitrate (28.7 g, 0.169 mol) in 50 ml of water and 25 ml of ethanol, followed by filtration, extraction of the basic solution, acidification with concentrated H_2SO_4, extraction with several portions of ether, drying ($MgSO_4$), reaction with diazomethane, and distillation gave 1.1 g (23%) of a mixture of methyl esters, bp 76–78° (14 mm).

Analysis of the Hydroformylation Mixture. The mixture of methyl esters was analyzed by gas chromatography (17% Carbowax 20M on Chromosorb P, 10 ft × 0.25 in., 125°). Comparison of retention times of authentic methyl esters with those of the methyl esters in the mixture relative to *n*-undecane indicated that the mixture consisted of methyl 4-methylheptanoate, methyl 2,3-dimethylhexanoate, methyl 3-ethylhexanoate, methyl 2-ethyl-2-methyl-2-pentanoate, and an unidentified ester in the relative ratio 91.5:5.0:2.3:0.7:0.5. The mixture was separated by preparative gas chromatography (25% Carbowax 20M on Chromosorb W, 10 ft × 3/8 in., 120°). The identification of methyl 4-methylheptanoate, methyl 2,3-dimethylhexanoate, and methyl 3-ethylhexanoate was confirmed by comparison of their $Eu(DPM)_3$-shifted nmr spectra with

(15) M. A. Bennett and R. Charles, *J. Amer. Chem. Soc.*, **94**, 666 (1972).

(16) I. Wender, H. W. Sternberg, S. Metlin, and M. Orchin, *Inorg. Syn.*, **5**, 190 (1957).

(17) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

(18) J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Amer. Chem. Soc.*, **87**, 5050 (1965).

authentic spectra. Analysis of the Eu(DPM)$_3$-shifted nmr spectra gave the location of the deuterium in these compounds (see Results).

3-Ethylhexanoic Acid. Following a procedure similar to that of Levene and Marker,[19] 18.6 g (53%) of 3-ethylhexanoic acid was prepared by the dropwise addition of 3-bromohexane (40 g, 0.244 mol) to a solution of diethyl malonate (41 g, 0.255 mol) and sodium (5.75 g, 0.25 mol) in 150 ml of dry ethanol: bp 119–120° (7 mm) (lit.[19] 106° (5 mm)); ir ν_{max}^{neat} 2950 (broad), 1710 cm^{-1}; nmr $\delta_{TMS}^{CDCl_3}$ 0.97 (m, 6 H, 2 CH_3), 1.36 (m, 6 H, 3 CH_2), 1.97 (m, 1 H, tert CH), 2.37 (d, 2 H, CHCH_2COOH), and 12.82 (s, 1 H, COOH).

Methyl 3-Ethylhexanoate. Addition of excess diazomethane (prepared from nitrosomethylurea and aqueous KOH) in ether to 3-ethylhexanoic acid (2.5 g, 0.017 mol) in 30 ml of dry ether followed by an aqueous work-up and distillation gave 1.7 g (63%) of methyl 3-ethylhexanoate: bp 65° (7 mm); ir ν_{max}^{neat} 2950, 1730 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 0.70–1.06 (m, 6 H, 2 CH_3), 1.06–1.60 (m, 6 H, 3 CH_2), 1.6–2.0 (m, 1 H, tert CH), 2.14 (d, 2 H, CHCH_2COOCH_3), 3.55 (s, 3 H, COOCH_3); nmr $\delta_{TMS}^{CCl_4}$ (35 mol % Eu(DPM)$_3$) 1.10–1.43 (t, 3 H, CH_3CH$_2$CH$_2$), 1.57–1.93 (t, 3 H, CH_3CH$_2$C), 2.00–2.70 (sextet, 2 H, CH$_3$CH_2CH$_2$), 2.73–3.42 (m, 4 H, 2 CH_2), 4.9–5.6 (m, 1 H, (CH$_3$)$_3$CH), 6.29 (d, 2 H, CHCH_2COOCH_3), and 7.30 (s, 3 H, COOCH_3).

2,3-Dimethylhexanoic Acid. According to a procedure similar to that of Kondakowa,[20] 20.4 g (34%) of 2,3-dimethylhexanoic acid was prepared by dropwise addition of 2-bromopentane (63.5 g, 0.42 mol) to a solution of diethyl methylmalonate (75 g, 0.43 mol) and sodium (9.7 g, 0.42 mol) in dry ethanol: bp 127–129° (16 mm) (lit. 86–87° (1 mm)); ir ν_{max}^{neat} 2950 (broad), 1710 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.65–1.55 (m, 13 H, 3 CH_3, 2 CH_2), 1.55–2.11 (m, 1 H, tert CH), 2.11–2.68 (m, 1 H, tert CH), and 12.65 (s, 1 H, COOH).

Methyl 2,3-Dimethylhexanoate. A mixture of diastereomers of methyl 2,3-dimethylhexanoate was prepared by the addition of diazomethane in ether to 2,3-dimethylhexanoic acid (5.0 g, 0.0347 mol) in ether, as above: bp 66–67° (11 mm); ir ν_{max}^{neat} 2950, 1735 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.73–1.55 (m, 13 H, 3 CH_3, 2 CH_2), 1.55–2.0 (m, 1 H, tert CH), 2.02–2.52 (m, 1 H, tert CH), and 3.55 (s, 3 H, COOCH_3); $\delta_{TMS}^{CCl_4}$ (30 mol % Eu(DPM)$_3$) 0.94–1.36 (t, 3 H, CH_3CH$_2$), 1.58–3.00 (m, 7 H, 1 CH_3, 2 CH_2), 2.54–2.78 (d of d, 3 H, CH_3CH (diastereomeric CH_3's)), 3.3–4.1 (m, 1 H, tert CH), 4.4–5.1 (m, 1 H, tert CH nearest carboxyl group), and 5.69 (s, 3 H, COOCH_3).

4-Methylheptanoic Acid. The procedure of Stork, *et al.*,[21] was followed to prepare ethyl 4-methyl-5-ketoheptanoate from the morpholine enamine of 3-pentanone and ethyl acrylate: bp 106.5–109° (8 mm) (lit.[21] 108–109° (10 mm)); ir ν_{max}^{neat} 1710, 1730 cm^{-1}. 4-Methylheptanoic acid was obtained by Huang-Minlon[22] modification of the Wolff–Kishner reduction of ethyl 4-methyl-5-ketoheptanoate: bp 130–132° (15 mm) (lit.[23] 132° (22 mm)); ir ν_{max}^{neat} 2900 (broad), 1700 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.67–1.10 (m, 6 H, 2 CH_3), 1.10–2.0 (m, 5 H, 2 CH_2, 1 CH), 2.3 (q, 2 H, CHCH_2CH$_2$), 3.67 (t, 2 H, CH$_2$CH_2COOH), and 10.68 (s, 1 H, COOH).

Methyl 4-Methylheptanoate. Methyl 4-methylheptanoate was prepared by the addition of diazomethane in ether to 4-methylheptanoic acid in ether, as above: bp 75–76° (11 mm); ir ν_{max}^{neat} 2960, 2870, 1740 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.70–1.09 (m, 6 H, 2 CH_3), 1.09–2.0 (m, 7 H, 3 CH_2, 1 CH), 2.20 (t, 2 H, CH$_2$CH_2COOCH_3), and 3.54 (s, 3 H, COOCH_3); nmr $\delta_{TMS}^{CCl_4}$ (40 mol % Eu(DPM)$_3$) 0.85–1.25 (t, 3 H, CH_3CH$_2$), 1.3–2.33 (m, 4 H, 2 CH_2), 1.66 (d, 3 H, CH_3CH), 2.8–3.35 (m, 1 H, tert CH), 4.57–5.83 (m, 2 H, CHCH_2CH$_2$), 7.10 (t, 2 H, CH$_2$CH_2COOCH_3), and 8.10 (s, 3 H, COOCH_3).

Methyl 2-Ethyl-2-methylpentanoate. 2-Methylbutanoic acid was prepared from 2-bromobutane, magnesium, and carbon dioxide according to the procedure of Burton and Cusic.[24] The crude acid was converted to the methyl ester with diazomethane (*vide supra*): bp 112–117° (lit.[24] 115.5–116°). Following a similar procedure of Hudson and Hauser,[25] 2.0 g (21%) of methyl 2-ethyl-2-methylpentanoate was obtained by the addition of *n*-bromopropane (9.25 g, 0.075 mol) to a mixture of methyl 2-methylbutanoate (7.0 g, 0.06 mol) and triphenylmethylsodium (0.06 mol) in ether: bp 72–78° (23–24 mm); ir ν_{max}^{neat} 2950, 1725 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.70–1.0 (m, 6 H, 2 CH_3), 1.05 (s, 3 H, CCH_3), 1.0–1.8 (m, 6 H, 3 CH_2), and 3.58 (s, 3 H, COOCH_3).

4-Methylheptanol. Following a similar procedure of Nystrom and Brown,[26] 3.8 g (80%) of 4-methylheptanol was prepared by the reduction of 4-methylheptanoic acid (5.0 g, 0.0347) mol) with lithium aluminum hydride (2.8 g, 0.074 mol); bp 101–104° (23 mm) (lit.[27] 85° (20 mm)); ir ν_{max}^{neat} 3320 (broad), 2900, 2860, 1050 (broad) cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.60–1.07 (m, 6 H, 2 CH_3), 1.07–1.8 (m, 8 H, 4 CH_2), 1.8–2.2 (m, 1 H, tert CH), 2.9–3.2 (broad s, 1 H, OH), and 3.5 (t, 2 H, CH$_2$CH_2OH).

2,3-Dimethylhexanol was prepared by the same method as above: bp 89–92° (16 mm); ir ν_{max}^{neat} 3340 (broad), 2940, 2900, 2860, 1025 (broad) cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.55–1.05 (m, 9 H, 3 CH_3), 1.05–2.1 (m, 6 H, 2 CH_2, 2 CH), 3.20 (s, 1 H, OH), and 3.38 (d, 2 H, CHCH_2OH).

3-Ethylhexanol was prepared by the same procedure as above: bp 92–94° (15 mm); ir ν_{max}^{neat} 3340 (broad), 2940, 2900, 2860, 1055 (broad) cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.55–1.05 (m, 6 H, 2 CH_3), 1.05–1.67 (m, 6 H, 3 CH_2), 3.34 (s, 1 H, OH), and 3.52 (d, 2 H, CHCH_2OH).

3-Ethylhexanal. Using the procedure of Collins, *et al.*,[28] 0.695 g (70%) of 3-ethylhexanal was obtained from the oxidation of 3-ethylhexanol (1.0 g, 7.7 mmol) with dipyridinechromium(VI) oxide (11.9 g, 46.2 mmol) in 200 ml of dry dichloromethane: bp 55° (8–9 mm); ir ν_{max}^{neat} 2700, 1725 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.65–1.10 (m, 6 H, 2 CH_3), 1.10–1.55 (m, 6 H, 3 CH_2), 1.67–2.1 (m, 1 H, tert CH), 2.14–2.38 (d of d, 2 H, CHCH_2CHO), and 9.65 (t, 1 H, CH$_2$CHO).

2,3-Dimethylhexanal was prepared from 2,3-dimethylhexanol by the same procedure as above: bp 61° (15–16 mm); ir ν_{max}^{neat} 2700, 1725 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.75–1.14 (m, 9 H, 3 CH_3), 1.14–1.55 (m, 4 H, 2 CH_2), 1.55–2.60 (m, 2 H, 2 tert CH), and 9.74 (d, 1 H, CHCHO).

4-Methylhexanal was prepared from 4-methylhexanol by the same procedure as above: bp 67–68° (17 mm); ir ν_{max}^{neat} 2700, 1725 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 0.60–1.06 (m, 6 H, 2 CH_3), 1.06–1.85 (m, 7 H, 3 CH_2, tert CH), 2.40 (t, 2 H, CH$_2$CH_2CHO), and 9.87 (t, 1 H, CH$_2$CHO).

(19) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **91**, 687 (1931).
(20) M. S. Kondakowa and M. M, Katznelson, *Dokl. Akad. Nauk SSSR*, **18**, 271 (1938); *Chem. Zentralbl.*, **109**, 4444 (1938).
(21) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).
(22) Huang-Minlon, *ibid.*, **68**, 2487 (1946).
(23) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **95**, 14 (1932).
(24) R. R. Burton and J. W. Cusic, *J. Amer. Chem. Soc.*, **65**, 264 (1943).
(25) B. E. Hudson and C. R. Hauser, *ibid.*, **62**, 2457 (1940).
(26) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 2548 (1947).
(27) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **103**, 303 (1933).
(28) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).