strong electronic coupling evidenced by the electron spin resonance spectrum of **2**.[11] In contrast, the cyclic voltammograms of **3** and **4** were very similar to that of cyclooctatetraene **1**,[12] indicative of the presence of predominantly electronically isolated rings, differing only in that the second wave was slightly split. The observed reduction potentials for these substrates are summarized in Table I.

Complete reduction of **1**–**6** could be achieved either by treatment with a 4-fold excess of either sodium or potassium metal in tetrahydrofuran or, more conveniently, by coulometrically monitored electrochemical reduction at a potential approximately 150 mV cathodic of the most negative reductive wave observed by cyclic voltammetry. A solution of each of the fully reduced substrates in dry, degassed DMF was then transferred to the previously described electrochemical cell.[5] Upon irradiation of the di- or tetraanion by a IR-filtered tungsten lamp ($\lambda > 400$ nm) of a thin, but opaque, layer (ca. 5-mm thick) of solution interspersed between a clean[13] indium tin oxide electrode and a Pyrex optical flat, an anodic photocurrent was observed. The magnitude of the observed photocurrent sensitized by **1**–**6** under constant light flux, obtained by correcting the observed current for the respective dark response, is listed in Table II.

The quantum efficiency for photocurrent sensitization (ca. $10^{-2}$%) is significantly lower for this series than has been reported recently by Grätzel and co-workers for sensitization by several Ru(bpy)$_3$ derivatives.[2a] The similarity of the photocurrents observed in **1**–**6** implies a comparable mechanism for photocurrent production throughout the series, probably in each case involving photoinduced electron injection from an anionic excited state into the indium tin oxide conduction band.[5] Apparently the electronic interaction between rings in **2** and **5** causes only a modest perturbation in the sensitization efficiency. Since parallel conformational variance and ion pairing effects control the electrochemical behavior of the hydrocarbons **1**–**5**, the absence of dramatic differences in their photosensitization efficiency is perhaps reasonable, with the observable current probably being governed instead by the availability of surface carrier traps at the metal oxide–electrolyte interface. Perhaps more surprising is the apparent similarity between the observed sensitization efficiency of these hydrocarbons and that of the tetrakisperfluorocyclobutano-fused derivative **6**, where the neutral hydrocarbon, the singly reduced radical anion, and the dianion are all planar.[10] In **6**, however, all three oxidation levels are stable, making the disproportionation equilibrium position of lesser consequence than the physical character of the electrode surface.

## Experimental Section

Bis(cyclooctatetraenyl)methane (**2**) and bis(cyclooctatetraenyl)ethane (**3**), prepared as previously described,[11] were purified by chromatography on silica gel (hexane). **2** (12% yield) as a pale yellow liquid: mass spectrum ($m/e$) 220.45 (P$^+$). **3** (36%) as a pale yellow viscous oil: mass spectrum ($m/e$) 234.20 (P$^+$).

**Bis(cyclooctatetraenyl)propane (4).** A solution of cyclooctatetraenylbromide[14] (2.1 g, 11 mmol) in 4 mL of dry THF was added dropwise to a stirred mixture of magnesium turnings (25 mmol) in 25 mL of dry THF at rt under N$_2$. As the reaction began, the solution was cooled with an ice bath as the addition continued over ca. 1.5 h. The resulting mixture was stirred at 0 °C for 2 h before being allowed to warm to rt, after which stirring continued for an additional 2 h. A 0.2-mL aliquot was removed from the mixture and was titrated with an HCl standard, showing 94% conversion of bromide. While being rigorously stirred while immersed in an ice bath, the remaining solution was treated by dropwise addition over 20 min with 1,3-dibromopropane (1.33 g, 6.6 mmol) in 30 mL of THF. The addition being complete, 0.34 mL of freshly prepared Li$_2$CuCl$_4$ in THF was added by syringe. The resulting mixture was stirred at 0 °C for 3 h and then at rt for an additional 18 h. Saturated NH$_4$Cl was then added, and the mixture was cooled to 0 °C. The organic layer was separated, washed with saturated NaHCO$_3$, dried over MgSO$_4$, filtered, and concentrated. Upon chromatographic purification on silica gel (hexane), **4** was isolated as a viscous yellow oil in 8% yield: $^1$H NMR (CDCl$_3$) 1.57 (pentet), 2.09 (t, 4 H), 5.77 (m, 14 H); $^{13}$C NMR (CDCl$_3$) 27.1, 37.0, 131.9 (overlapping peaks), 144.2; mass spectrum ($m/e$) 248.00 (P$^+$).

**Electrochemical Measurements.** Cyclic voltammetric measurements were conducted as 0.01 M solutions in dry DMF containing 0.1 M tetrabutylammonium perchlorate in a standard two-compartment cell with a Pt wire working electrode, a Pt disk counter electrode, and a silver wire quasi-reference electrode. The reported potentials are referenced with respect to the reported value for **1**[12] or **5**.[9] The cell potential was controlled with a Princeton Applied Research electrochemical system comprising a Model 173 potentiostat, a Model 175 universal programmer, and a Model 179 digital coulometer, with traces recorded on a Houston Instruments 2000 x/y recorder.

Photocurrent measurements were made under an argon blanket as previously described, in a cell identical to that employed earlier,[5] on a Fluka microammeter. Quantum efficiencies were crudely estimated by taking a ratio of the observed photocurrent to the incident light flux, measured by a power meter at the surface of the photoelectrochemical cell.

**Acknowledgment.** The financial support of those portions of this work conducted at the University of Texas was provided by the U.S. Department of Energy, Office of Basic Energy Sciences, and that at the University of Miami by the National Science Foundation. R.L.S.'s participation in this program was generously supported by a faculty summer research supplement provided by the National Science Foundation.

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# Excellent Regiochemical Control in the Hydroformylation of $\alpha,\beta$-Unsaturated Esters Catalyzed by Zwitterionic Rhodium Complexes and 1,4-Bis(diphenylphosphino)butane

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One of the most thoroughly investigated reactions in homogeneous catalysis is the hydroformylation of olefins. Recently, one of us[1] found that the zwitterionic rhodium complex **1** is an excellent catalyst for this process, with high regioselectivity observed for the branched (eq 1) or linear (eq 2) aldehyde depending on the nature of the reactant. However, poor regiochemical control was found during attempts to apply the reaction to $\alpha,\beta$-unsaturated esters such as methyl acrylate and methyl methacrylate.

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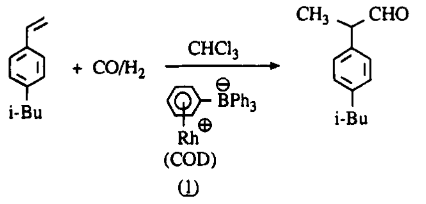
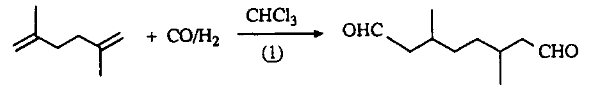


(eq. 1)



(eq. 2)

We are aware of the beneficial influence of 1,4-bis(diphenylphosphino)butane (dppb) as an added ligand in metal-catalyzed processes. In some cases, its presence enables reactions to occur which do not otherwise proceed,[2,3] and occasionally dppb can alter the regioselectivity of a reaction.[4,5] We now wish to report that the use of the zwitterionic rhodium complex, in conjunction with dppb, as a catalytic system for the hydroformylation of $\alpha,\beta$-unsaturated esters results in excellent regioselectivity for the branched-chain aldehydic ester.

Treatment of ethyl acrylate with synthesis gas (1:1 $CO/H_2$) and a catalytic amount of 1 (100:1 ratio of substrate/1) in methylene chloride, for 12 h at 80 °C and a total pressure of 600 psi, afforded the branched-chain and linear aldehydes in a 57/43 ratio (51% yield). However, repetition of the experiment in the presence of dppb (2:1 ratio of dppb/1), not only gave the aldehydic esters in appreciably higher yield (79%, see Table I for results) but the ratio of branched to linear products was 49:1. The hydroformylation process was regiospecific in the case of *sec*-butyl acrylate, and excellent regioselectivity was found when the 1,1-disubstituted olefinic esters, methyl methacrylate, or $\alpha$-methylene-$\gamma$-butyrolactone (affords 2) were employed as substrates. Ethyl crotonate, containing a 1,2-disubstituted double bond, affords 3 in 60–68% yield and excellent regioselectivity irrespective of the stereochemistry of the reactant.

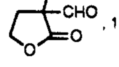
$$\underset{\substack{\text{cis}\\\text{trans}}}{CH_3CH{=}CHCOOC_2H_5}\xrightarrow[\substack{130\ °C,\ 12\ h,\ CH_2Cl_2\\60\%\ \text{yield (from cis)}\\68\%\ \text{yield (from trans)}}]{CO/H_2,\ 1,\ \text{dppb}}$$

$$\underset{(3)}{OHCC(C_2H_5)HCOOC_2H_5} + OHCC(CH_3)HCH_2COOC_2H_5$$

$$\begin{matrix}99 & : & 1\\98 & : & 2\end{matrix}$$

Let us compare the present results with existing literature on the regioselectivity of the hydroformylation of $\alpha,\beta$-unsaturated esters. Of particular note is the recent publication by Neibecker and Réau[5] on the use of rhodium phosphole and phosphanorbornadienes (from $[Rh(CO)_2Cl]_2$ and added ligand) as catalysts for the hydroformylation of ethyl acrylate. Although the reaction is regiospecific, an investigation was not conducted on the scope and limitations using a variety of $\delta,\beta$-unsaturated esters. The work of Neibecker and Réau[5] is derived from the previous study by Tanaka and co-workers[6] who used the same rhodium catalyst but with added bidentate phosphine ligands such as dppb. The regiochemistry control of the zwitterionic complex–dppb catalytic system is consistently superior to that of $[Rh(CO)_2Cl]_2$–dppb or other bidentate phosphines. Furthermore, 1 compares favorably with the well-known hydridorhodium catalyst $HRh(CO)(PPh_3)_3$, both used with dppb (i.e., ethyl acrylate with $HRh(CO)(PPh_3)_3$-dppb affords 34% branched and 13% linear aldehydes, together with 53% ethyl propionate).[7] In conclusion, 1–dppb catalyzes the hydroformylation of $\alpha,\beta$-unsaturated esters to give aldehydic esters in good yields and with high regiochemical control.

**Table I. Hydroformylation of $\alpha,\beta$-Unsaturated Esters Catalyzed by 1–dppb**

| ester | temp (°C) | time (h) | isolated yield (%) | product distribn[a] |
|---|---|---|---|---|
| ethyl acrylate | 80 | 12 | 79 | $CH_3C(CHO)HCOOC_2H_5$, 98[b]<br>$OHCCH_2CH_2COOC_2H_5$, 2 |
| *sec*-butyl acrylate | 80 | 12 | 76 | $CH_3C(CHO)HCOOC(CH_3)$-$HC_2H_5$, 100[c] |
| methyl methacrylate | 80 | 12 | 20 | $(CH_3)_2C(CHO)COOCH_3$, 97<br>$OHCCH_2C(CH_3)$-$HCOOCH_3$, 3 |
|  | 130 | 24 | 75 | $(CH_3)_2C(CHO)COOCH_3$, 96<br>$OHCCH_2C(CH_3)$-$HCOOCH_3$, 4 |
| $\alpha$-methylene-$\gamma$-butyrolactone | 130 | 24 | 56 |  , 100<br>(2) |
| *cis*-ethyl crotonate | 130 | 12 | 60 | $OHCC(C_2H_5)HCOOC_2H_5$, 99<br>$OHCC(CH_3)HCH_2COO_2H_5$, 1 |
| *trans*-ethyl crotonate | 130 | 12 | 68 | $OHCC(C_2H_5)HCOOC_2H_5$, 98<br>$OHCC(CH_3)$-$HCH_2COOC_2H_5$, 2 |

[a] All aldehydic esters are known compounds (with one exception, see Experimental Section) and were identified by comparison of spectral data with authentic materials or with literature results. [b] Enol content is 40% in $CDCl_3$ and 100% in DMSO-$d_6$ (NMR determination). [c] 42% enol tautomer in $CDCl_3$.

## Experimental Section

**General Procedure for the Hydroformylation of $\alpha,\beta$-Unsaturated Esters.** A mixture of the ester (4.0 mmol), 1 (0.040 mmol),[8] and dppb (0.090 mmol) in $CH_2Cl_2$ (10 mL) was pressurized to 600 psi using 1:1 $CO/H_2$. After reaction for 12–24 h at 80–130 °C (see Table I for details), the mixture was passed through a silica gel column, and pure products were obtained by thin-layer chromatography with 7:3 hexane/ethyl acetate.

Compound 2 is new: $^1H$-NMR ($CDCl_3$) $\delta$ 1.52 (s, 3 H, $CH_3$), 2.17 (m, 1 H, CH of $CH_2$), 2.83 (m, 1 H, CH, of $CH_2$), 4.33 (m, 2 H, $CH_2O$), 9.56 (s, 1 H, CHO). Also characterized by reaction of the lactonic aldehyde with benzylamine to give the corresponding Schiff base ($RCH{=}NCH_2Ph$): $^1H$-NMR ($CDCl_3$) $\delta$ 1.50 (s, 3 H, $CH_3$), 2.15 (m, 1 H, CH of ring $CH_2$), 2.91 (m, 1 H, CH of ring $CH_2^-$), 4.45 (t, 2 H, $CH_2O$), 4.69 (s, 2 H, $PhCH_2$), 7.35 (m, 5 H, Ph), 7.82 (s, 1 H, CH=N) ppm; $^{13}C$-NMR ($CDCl_3$) $\delta$ 20.87 ($CH_3$), 32.63 ($CH_2CH_2O$), 48.50 (saturated quaternary C), 64.13, 65.87 ($CH_2Ph,CH_2O$), 127.08, 127.61, 128.50 (aromatic CH), 138.59 (aromatic C), 163.25 (CN), 178.37 (CO) ppm; MS (*m/e*) 217 $[M]^+$. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96. Found: C, 71.60; H, 7.01.

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**Registry No.** **2**, 141046-47-1; $CH_2{=}CHCO_2Et$, 140-88-5; $CH_2{=}CHCO_2Bu$-s, 2998-08-5; $CH_2{=}C(CH_3)CO_2Me$, 80-62-6; (*Z*)-$CH_3CH{=}CHCO_2Et$, 6776-19-8; (*E*)-$CH_3CH{=}CHCO_2Et$, 623-70-1; $CH_3CH(CHO)CO_2Et$, 27772-62-9; $CH_3CH(CHO)CO_2Bu$-s, 141046-48-2; $OHCC(CH_3)_2CO_2Me$, 13865-20-8; $CH_3CH_2CH(CHO)CO_2Et$, 36873-42-4; $OHC(CH_2)_2CO_2Et$, 10138-10-0; $OHCCH_2CH(CH_3)CO_2Me$, 13865-21-9; $OHCCH(CH_3)CH_2CO_2Et$, 54998-57-1; $CH_3C({=}CHOH)CO_2Et$, 54843-13-9; $CH_3C({=}CHOH)CO_2Bu$-s, 141046-49-3; (COD)Rh($BPh_4$) complex, 31974-01-3; α-methylene-δ-butyrolactone, 547-65-9; 3-methyl-2-oxo-3-furancarboxaldehyde, 55341-13-4; dppb, 7688-25-7.

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# A New and Simple Synthesis of Mosher's Acid

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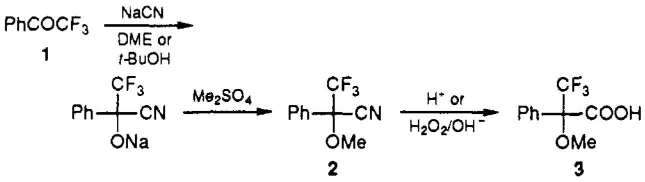
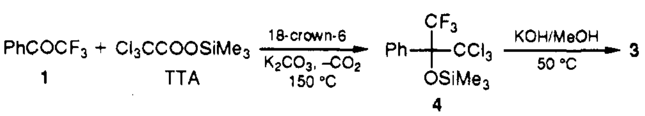
A frequently used chiral reagent for the determination of enantiomeric purity of chiral alcohols and amines[1] is α-methoxy-α-(trifluoromethyl)phenylacetic acid, also known as Mosher's acid.[2] This compound has been synthesized by reaction of α,α,α-trifluoroacetophenone (**1**) with sodium cyanide in 1,2-dimethoxyethane (DME) followed by alkylation with dimethyl sulfate to give the nitrile **2** and finally hydrolysis of **2**, first to the amide and then to the acid **3**.[2] More recently, a modified synthesis of **3**[3]



was developed, with minor improvements realized over the original preparation (i.e., use of *tert*-butyl alcohol instead of DME and use of alkaline hydrogen peroxide for the hydrolysis of **2**). While these methods afford Mosher's acid in quite good yield, they require the use of toxic sodium cyanide and dimethyl sulfate. We now report a new method for the preparation of Mosher's acid, based on the addition of trimethylsilyl trichloroacetate (TTA) to **1** and subsequent hydrolysis of **4** to **3**. This may be done without isolation of **4**, thus providing an efficient one-flask procedure for the synthesis of **3**.



TTA, a known[4,5] reagent for the trichloromethylation of ketones, has been prepared by silylation of trichloroacetic acid with hexamethyldisilazane,[6] hexamethyldisiloxane,[7] or trimethylchlorosilane.[8] Disadvantages of these methods include concurrent formation of side products[6,7] and long reaction times.[8] We have found that solid–liquid[9] phase transfer catalyzed (PTC) reaction of sodium trichloroacetate with chloromethylsilane is a simple, mild, and convenient route to TTA. When a mixture of $CCl_3COONa$ (0.10 mol), $Me_3SiCl$ (0.12 mol), and 18-crown-6 (5 mmol) in benzene was stirred for 4 h at room temperature, TTA was obtained in 75% yield of pure material. The yield increased to 83% when the reaction was run for 12 h. Other phase-transfer agents, including quaternary ammonium salts, a polymer bound phosphonium salt, poly(ethylene glycol) (PEG-400), and tris(polyoxaheptyl)amine (TDA-1) were much less effective in this regard (Table I). Of these it is noteworthy that polymer-anchored tributylhexylphosphonium bromide can be reused without a loss in activity.

**Table I. Phase Transfer Catalyzed Silylation of Sodium Trichloroacetate[a]**

| phase-transfer agent | reaction time, h | % TTA[b] |
|---|---|---|
| 18-crown-6 | 4 | 75 |
| | 12 | 83 |
| $Bu_4N^+HSO_4^-$ | 24 | 2[c] |
| Adogen 464 | 24 | 19 |
| $(n\text{-}C_8H_{17})_4N^+Br^-$ | 24 | 48 |
| Ⓟ-$(CH_2)_6PBu_3^+Br^-$ | 24 | 45 (47)[d] |
| PEG-400 | 24 | 23 |
| TDA-1 | 24 | 26 |

[a] Molar ratio of $Cl_3CCOONa$:$Me_3SiCl$:catalyst was 1.0:1.2:0.05, rt in benzene. [b] Isolated yield of pure material. [c] GC yield. [d] Yield after reuse of phase-transfer catalyst.

Treatment of TTA with **1** in the presence of catalytic quantities of 18-crown-6 and $K_2CO_3$, for 30 min at 150 °C afforded **4** in 83% yield. Dibenzo-18-crown-6 and dicyclohexano-18-crown-6 can be used in place of 18-crown-6 with similar results, and TDA-1 was also useful, but a longer reaction time (3 h) was necessary in this case. Methanolic potassium hydroxide was used to effect simultaneous disilylation, hydrolysis, and methylation, resulting in the conversion of **4** to **3** in 79% yield. This method has been useful for the preparation of α-methoxymandelic acid from phenyl(trichloromethyl)carbinol.[10]

## Experimental Section

**Trimethylsilyl Trichloroacetate (TTA).** To a suspension of sodium trichloroacetate (18.54 g, 0.10 mol) in benzene (30 mL) containing 18-crown-6 (1.32 g, 5.0 mmol) was added chlorotrimethylsilane (12.84 g, 0.118 mmol), and the reaction mixture was stirred at rt for 12 h. The solution was filtered, and benzene and excess $Me_3SiCl$ were removed by rotary evaporation. Vacuum distillation of the residue afforded 19.65 g (83%) of TTA, bp 42–43 °C (1 mmHg) [lit.[10] bp 69 °C (10 mmHg)].

**α-Methoxy-α-(trifluoromethyl)phenylacetic Acid (3).** A mixture of **1** (1.74 g, 10 mmol), TTA (2.83 g, 12 mmol), 18-crown-6 (0.132 g, 0.5 mmol), and $K_2CO_3$ was stirred at 150 °C until the evolution of $CO_2$ was complete (i.e., 30 min). If required, **4** can be isolated by vacuum distillation [2.98 g (82% yield); bp 65–67 °C (0.2 mmHg); $^1H$ NMR ($CDCl_3$) δ 0.25 (s, 9 H, $SiMe_3$), 7.3–7.8 (m, 5 H, Ph) ppm; MS *m/e* 247 [M − $CCl_3$]$^+$]. Compound **4**, or the reaction mixture above, is dissolved in methanol (15 mL) and warmed to 60 °C. A solution of 5.6 g (0.1 mol) of KOH in methanol (50 mL) was added dropwise, and stirring was continued

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