63243-77-6; **4j**, 79043-92-8; **4k**, 55296-87-2; **4l**, 72368-51-5; **4m**, 72368-52-6; **5a**, 72573-64-9; **5b**, 72556-88-8; **8a**, 72592-61-1; **8b**, 72592-62-2; **8c**, 72592-63-3; **8d**, 72592-64-4; **8e**, 79043-93-9; **8f**, 72592-65-5; **8g**, 72592-66-6; **8h**, 72592-67-7; **9a**, 72592-69-9; **9b**, 79043-94-0; **9c**, 79043-95-1; **9d**, 79043-96-2; **9e**, 79043-97-3; **9f**, 79043-98-4; **9g**, 79043-99-5; **9h**, 79044-00-1; **9i**, 79044-01-2; **9j**, 79044-02-3; **9k**, 29124-68-3; **9l**, 68882-99-5; **9m**, 79044-03-4; **9n**, 79044-04-5; **9o**, 68883-00-1; **9p**, 79044-05-6.

Asymmetric Hydroformylation of Vinyl Acetate with DIOP-Type Ligands

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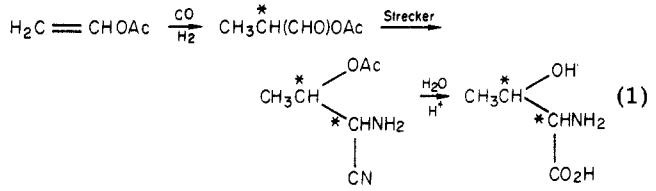
The rhodium-catalyzed hydroformylation of vinyl acetate and related esters was carried out in the presence of chiral phosphine ligands of the DIOP type to give the corresponding optically active 2-(acyloxy)propanal, a precursor for the amino acid threonine. Ligand structure and the ligand/metal ratio were the primary factors controlling asymmetric induction; temperature, CO pressure, and solvent polarity had minor effects. The highest induction efficiencies, up to 51% ee, were obtained with the 5*H*-dibenzophospholyl derivative of DIOP[7] (DIPHOL, **1e**).

The synthesis of optically active compounds by asymmetric catalysis has gene rated increasing interest in recent years. Following success in achieving high efficiencies in asymmetric hydrogenation,[1] attention has turned to applying asymmetric catalysis to other reactions such as hydroformylation.[2-5] Asymmetric hydroformylation of vinyl acetate, for example, is particularly attractive as it leads to chiral 2-acetoxypropanal, a precursor for the



(1)

Strecker synthesis of the amino acid threonine.[6] For simple hydrocarbon olefins, efficiencies of asymmetric induction for hydroformylation have been modest, with maximum enantiomeric excesses (ee) reaching about 30% with DIOP[7]-type ligands.[8-11] Higher optical yields, in the 40% range, have been reported for hydroformylation of styrene and its derivatives with DIPHOL.[12-14] Asymmetric hydroformylation of vinyl acetate has been studied[15,16], the highest optical yield reported being 32%, achieved by using DIOP.[16] In this paper, we report on the rhodium-catalyzed hydroformylation of vinyl acetate and related esters in the presence of DIOP and several new DIOP derivatives which afford improved asymmetric induction efficiencies.

Results

Hydroformylation of vinyl acetate was carried out in the presence of rhodium catalysts complexed with a series of DIOP-type ligands at various ligand-to-rhodium ratios and under a variety of pressure and temperature conditions. In general, catalyst complexes were prepared in situ from Rh(COD)acac and the desired DIOP analogue although in the case of DIOP itself and DIPHOL discreet rhodium complexes were prepared independently and charged into the reaction mixture. The effects of ligand structure and reaction variables on the reaction rate and asymmetric induction (enantiomeric excess, ee) are summarized in Table I.

The major product was 2-acetoxypropanal produced with selectivities generally in the range of 75–95%. Minor amounts of the 3-acetoxy isomer were also produced; this partly decomposed under the conditions of reaction to give acetic acid and acrolein which was hydrogenated to propanal under the conditions of the reaction.

The extent of asymmetric induction varied widely and depended primarily on the ligand structure and the lig-

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(7) DIOP is the name coined for *trans*-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.[2a] The Chemical Abstracts nomenclature is adopted in this paper for DIOP and derivatives; thus, DIOP is *trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane.

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0022-3263/81/1946-4422$01.25/0

Table I. Hydroformylation of Vinyl Acetate with DIOP and Derivatives[a]

catalyst	L	ratio of L/Rh	temp, °C	P, psig	rate, mol/L/h	ee,[b] %	config ligand	config prod
Rh(COD)acac + L	1a	1	80	500	0.77	2	R,R	S
		4	70	250	0.15	40		
Rh(NBD)L·B(Ph)$_4$ + L	1a	1	80	500	0.52	12	S,S	R
		3	80	250	0.52	33		
		3	80	500	0.34	30		
		3	80	1000	0.52	32		
		3	80	250	0.59	34[c]		
		3	80	250	0.28	29[d]		
		4	80	250	0.76	32		
Rh(COD)acac + L	1b	3	80	250	0.26	6	R,R	S
		4	80	500	0.38	5		
		5	80	500	0.26	5		
Rh(COD)acac + L	1c	2	60	150	0.19	15	R,R	S
		3	70	250	0.19	39		
		3	70	150	0.89	38		
		3	80	250	0.53	39		
		4	80	250	0.30	39		
		4	80	500	0.33	39		
		5	80	500	0.20	39		
Rh(COD)acac + L	1d	3	50	150	0.25	42	R,R	S
		3	60	150	0.73	38		
		3	80	150	3.51	24		
		3	80	250	1.37	30		
		6	80	250	2.07	29		
Rh(COD)acac + L	1e	3	70	250	0.30	14	R,R	R
		3	80	250	0.99	6		
		4	70	250	0.22	38		
		4	80	150	0.20	38		
		4	80	250	0.86	35		
		4	80	500	0.38	41		
		4	80	1000	0.32	46		
		4	90	1000	0.90	39		
		5	80	250	0.21	42		
		5	80	500	0.23	44		
		5	80	1000	0.37	38		
		5	90	250	1.03	40		
		6	80	500	0.26	51		
		6	90	250	0.45	38		
		8	90	250	0.36	43		
Rh(COD)L·ClO$_4$ + L	1e	1	80	500	0.24	2	R,R	R
		3	70	250	0.07	38		
		5	90	250	0.25	37		
Rh(COD)acac + L	1f	3	80	250	0.75	5	R,R	R
		4	70	250	0.35	16		
		4	80	250	0.95	17		
		5	80	250	0.95	17		
		6	70	100	0.25	16		
		6	70	250	0.35	18		
		6	70	500	0.19	18		
		6	80	250	1.28	18		
Rh(COD)acac + L	2	2	65	150	0.16	22	R,R	S
		2	70	150	0.48	15		
		3	70	150	0.30	25		
		3	80	150	0.68	24		
		3	80	250	0.49	27		
		3	80	500	0.23	28		
		3	90	150	1.44	23		
		4	80	150	0.62	25		
		4	80	250	0.40	29		
		4	100	250	1.18	18		
		5	80	250	0.25	26		

[a] Rhodium, 8×10^{-4} M; vinyl acetate, 3.45 M; benzene solvent. CO–hydrogen ratio of 44:56. [b] Enantiomeric excess. [c] Cyclohexane solvent. [d] Tetrahydrofuran solvent.

and-to-rhodium ratio. Temperature exerted a smaller effect with lower temperatures favoring a higher ee as expected. For most ligands, the enantiomeric excess increased with an increasing ligand-to-rhodium ratio, usually reaching a maximum at a ratio of 3:1 or 4:1.

Reactions which were stopped at various stages of completion gave essentially identical ee values at all stages. In addition, a test was made to determine if racemization of initially formed product might be occurring during the reaction. A sample of 2-acetoxypropanal having 35% ee was subjected for 8 h to reaction conditions which would have produced 6% ee on starting from vinyl acetate; the recovered product had 35% ee, demonstrating that no racemization had occurred.

Results with DIOP (1a) using the Rh(NBD)(DIOP)·B(C_6H_5)$_4$ complex confirmed earlier reports,[16] with a maximum observed ee of 33%. This could be increased to 40% with Rh(COD) acac plus DIOP by lowering the

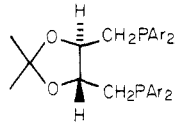
Table II. Hydroformylation of Vinyl Propionate and Benzoate with DIOP and Derivatives[a]

$$RCO_2CH{=}CH_2 \xrightarrow[H_2]{CO} RCO_2CH(CHO)CH_3$$

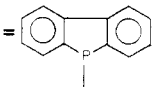
catalyst	ligand	ratio of L/Rh	temp, °C	P, psig	rate, mol/L/h	ee,[b] %	config ligand	config prod
			R = CH_3CH_2					
Rh(NBD)(DIOP)·$B(C_6H_5)_4$ + L	1a	3	80	250	0.34	29	*S,S*	*R*
Rh(COD)acac + L	1c	3	80	250	0.35	36	*R,R*	*S*
Rh(COD)acac + L	1d	3	60	150	0.59	33	*R,R*	*S*
Rh(COD)acac + L	1e	4	80	250	0.37	32	*R,R*	*R*
Rh(COD)acac + L	2	3	80	250	0.35	18	*R,R*	*S*
			R = C_6H_5					
Rh(NBD)(DIOP)·$B(C_6H_5)_4$ + L	1a	3	80	250	0.38	30	*S,S*	*R*
Rh(COD)acac + L	1e	4	80	1000	0.30	12	*R,R*	*R*

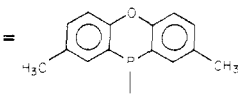
[a] Rhodium, 8×10^{-4}; vinyl ester, 3.45 M; benzene solvent. CO–hydrogen ratio of 44:56. [b] Enantiomeric excess.

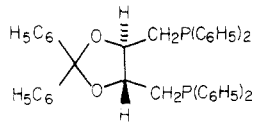
temperature from 80 to 70 °C, although the reaction rate under these conditions was quite slow.



1a, Ar = C_6H_5 (DIOP)
b, Ar = 1-$C_{10}H_7$ (1-NA-DIOP)
c, Ar = 2-$C_{10}H_7$ (2-NA-DIOP)
d, Ar = *m*-$CF_3C_6H_4$ (*m*-CF_3DIOP)

e, PAr_2 =  (DIPHOL)

f, PAr_2 =  (DMPP-DIOP)



2 (DIPH-DIOP)

Structural variations at the posterior of the DIOP structure had little effect on induction efficiency. Thus, replacement of the methyl groups at the 2-position[7] of the dioxolane ring with bulkier phenyl groups to give **2** resulted in a slight decrease in asymmetric induction. Similar results have been observed in asymmetric hydrogenation with comparable ligands.[17]

Sustitution of CF_3 groups at the meta position of the phosphorus-bound phenyl groups of DIOP to give **1d** effected almost no change in the ee although the rates increased 3–8-fold, probably as a result of electronic effects.

Further increase in the steric bulk of substituents at phosphorus had a dramatic effect. 1-Naphthyl groups, **1b**, caused a decrease in ee to 5–6%. By contrast, 2-NA-DIOP (**1c**) exhibited somewhat superior efficiencies compared to those of DIOP.

The dibenzophosphole analogue, DIPHOL (**1e**), afforded the highest induction of any of the ligands studied: 51% ee at 80 °C with a ligand-to-rhodium ratio of 6:1. At higher ratios, rates became too slow at this temperature for convenient study. Unlike the other ligands which reach a plateau of induction efficiency at a ligand-to-rhodium ratio of 3:1 or 4:1, DIPHOL showed increasing efficiencies up to a ratio of at least 6:1. In addition, DIPHOL gave 2-acetoxypropanal with a configuration opposite to that provided by DIOP and ligands **1b–d**; i.e., (*R,R*)-DIPHOL gave *R* products, whereas (*R,R*)-DIOP gave *S* products. The phenoxaphosphine **1f** shared this distinction, although it was only about half as effective as DIPHOL in inducing asymmetry.

A very slight solvent polarity effect was noted in the hydroformylation of vinyl acetate in the presence of DIOP. Thus, tetrahydrofuran gave a slightly lower ee than benzene while cyclohexane afforded a slightly higher ee. This effect is consistent with a system in which solvent, particularly polar solvent, competes with ligand for coordinating sites.

Asymmetric hydroformylation of vinyl propionate gave results comparable to those obtained with the acetate. Vinyl benzoate gave similar results with DIOP but gave only 12% ee with DIPHOL as compared to 46% ee obtained with vinyl acetate under identical conditions. Results with vinyl propionate and benzoate are summarized in Table II.

Discussion

Asymmetric hydroformylation affords generally lower induction efficiencies than asymmetric hydrogenation. This might be expected as hydroformylation is a more difficult reaction, involving more steps and requiring higher temperatures. A further complicating factor is the presence of the strong carbon monoxide ligand which competes with chiral ligand and the substrate for coordination sites on the metal center.

Asymmetric hydroformylation of vinyl esters proceeds with generally higher efficiencies than with hydrocarbon olefins. In fact, the 51% ee reported here for the hydroformylation of vinyl acetate with DIPHOL is the highest for any asymmetric hydroformylation reported to date, although still below the 90% level considered necessary for practical synthetic utility, often readily achievable in hydrogenation.[1] The larger induction observed with vinyl esters may be due to their greater ability to complex with the metal, perhaps functioning as bidentate ligands by coordination through the carbonyl oxygen as well as through the olefin doublebond.[15] The high ee's noted for asymmetric hydrogenation of (acylamino)acrylic acids, for example, have been ascribed in part to their ability to function as tridentate substrates.[1a,18]

(17) Dang, T. P.; Poulin, J. C.; Kagan, H. B. *J. Organomet. Chem.* **1975**, *91*, 105.

(18) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *Adv. Chem. Ser.* **1974**, *No. 132*, 274.

The most obvious explanation for the observation of increasing enantioselectivity with increasing ligand-to-rhodium ratio is that we are dealing with equilibria between species having differing induction efficiencies. One possibility is that carbon monoxide competes so effectively with phosphine ligand for coordination sites that some hydroformylation is occurring with species devoid of phosphine ligands, the concentration of such species being dependent on ligand concentration. Another possibility is that the expected bidentate complex[19] is present but in equilibrium with a more effective complex having a second ligand, perhaps complexed in a monodentate fashion.[15]

The enantioselective efficiencies of the DIOP-type ligands can be roughly correlated with their structures. CPK molecular models of the metal bidentate complexes of DIOP, *m*-CF_3-DIOP (**1d**) and DIPH-DIOP (**2**), show comparable steric requirements at the metal center, in agreement with their comparable efficiencies in asymmetric hydroformylation. 2-NA-DIOP (**1c**) is noticeably more crowded than DIOP, but the alternate edge–face configuration[1a,20] of the aromatic rings is easily accommodated. The slightly higher induction observed with this ligand compared to DIOP is consistent with the larger faces presented by the naphthyl rings.

On the other hand, the 1-NA-DIOP–rhodium bidentate complex is severely crowded, so much so that its CPK model is difficult to construct. The low ee observed with this ligand may be due to the 1-naphthyl groups being so large and hindering as to mask the effect of asymmetry in the molecule. An alternative explanation is that the ligand is only able to function in a monodentate fashion, forming a less efficient complex.

The higher ee obtained with DIPHOL relative to DIOP is consistent with results obtained for hydroformylation and hydroesterification of simple olefins[12-14] and enamides.[21] As in the case of 2-NA-DIOP, it is tempting to ascribe the greater inductive ability of the DIPHOL ligand to the larger, rigid, planar surfaces of the dibenzophospholyl groups which may help to orient the substrate molecule. However, this explanation fails to explain the results for DMPP-DIOP (**1f**). Like DIPHOL, DMPP-DIOP has large planar groups, shows rate enhancement relative to DIOP,[22] and gives a product with the opposite configuration to that of DIOP. However, asymmetric induction was distinctly inferior with DMPP-DIOP, underscoring the subtlety of the factors controlling asymmetric induction.

Experimental Section

General Methods. Melting points are corrected. ^1H NMR spectra were obtained on a Varian T-60 except as noted. ^{31}P NMR spectra were obtained on a Bruker WP-60; chemical shifts upfield relative to H_3PO_4 are assigned positive values.

Materials. (*S,S*)-(+)- and (*R,R*)-(−)-*trans*-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane[7] (**1a**, DIOP) and (−)-*trans*-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-di-*p*-tosylbutane (both from Strem Chemicals, Inc.) as well as vinyl acetate (Eastman), vinyl benzoate, and vinyl propionate (Pfaltz and Bauer) were used as received. Rh(1,5-COD)acac,[23] Rh(NBD)-[(+)-DIOP]·$B(C_6H_5)_4$,[24] and (R,R)-(−)-*trans*-4,5-bis[(5*H*-dibenzophospholyl)methyl]-2,2-dimethyl-1,3-dioxolane[17] [**1e**; mp 192–193 °C, $[\alpha]^{20}_D$ −66.03° (*c* 2.0, C_6H_6)] were all prepared by known methods.

Rh(1,5-COD)[(*S,S*)-*trans*-4,5-bis[(5*H*-dibenzophospholyl)methyl]-2,2-dimethyl-1,3-dioxolane]ClO_4. The complex was prepared in 82% yield from Rh(1,5-COD)acac and the phosphorus ligand by the method of Schrock and Osborn:[23] Anal. ($C_{39}H_{40}ClO_6P_2Rh$) C, H, Cl, Rh.

Bis(1-naphthalenyl)phosphine Oxide. The reaction of 2.2 molar equiv. of (1-naphthalenyl)magnesium bromide (slurry in ether) with the sodium salt of diethyl phosphite, followed by the usual workup procedure,[27] afforded the phosphine oxide: 81% yield; mp 166–168 °C (C_6H_6–hexane) (lit.[28] mp 79 °C); ^1H NMR ($CDCl_3$) τ 1.25 (d, 1 H, J = 490 Hz, PH), 2.17 (m, 14 H, aromatic); ^{31}P NMR ($CDCl_3$) σ -17.76 (2t, J_1 = 17.1 Hz, J_2 = 481 Hz). Anal. ($C_{20}H_{15}OP$) C, H, P.

Bis(2-naphthalenyl)phosphine Oxide. Reaction of 2 equiv of (2-naphthalenyl)magnesium bromide with sodium diethyl phosphite in ether was carried out as described above for the 1-naphthalenyl analogue: mp 112–113 °C (C_6H_6–cyclohexane); ^1H NMR ($CDCl_3$) τ 1.72 (d, 1 H, J = 477 Hz, PH), 2.25 (m, 14 H, aromatic); ^{31}P NMR ($CDCl_3$) σ −20.98 (d, J = 474 Hz). Anal. ($C_{20}H_{15}OP$) C, H, P.

Bis(α,α,α-trifluoro-3-tolyl)phosphine Oxide. The phosphine oxide was prepared in 79% yield by reaction of 3 equiv of (α,α,α-trifluoro-3-tolyl)magnesium bromide with diethyl phosphite in ethyl ether: mp 63–65 °C (lit.[29] mp 53.5–54.5 °C); ^1H NMR ($CDCl_3$) τ 1.50–2.70 (m, 8 H, aromatic), 2.7 (d, 1 H, J = 339 Hz, PH).

Bis(1-naphthalenyl)phosphine. Reduction of bis(1-naphthalenyl)phosphine oxide with an equimolar amount of diphenylsilane in the standard manner[26] afforded the phosphine: 85% yield; bp 205–210 °C (0.10 mm); mp 91–97 °C; ^1H NMR (C_6D_6) τ 1.67 (m, 2 H, aromatic), 2.67 (m, 12 H, aromatic), 4.37 (d, 1 H, J = 220 Hz, PH); ^{31}P NMR ($CDCl_3$) σ 62.58 (d, J = 22 Hz). Anal. ($C_{20}H_{15}P$) C, H, P.

Bis(2-naphthalenyl)phosphine. Diphenylsilane reduction of the phosphine oxide as described above afforded the phosphine: 86% yield; bp 208–213 °C (0.3 mm); mp 94–96 °C; ^1H NMR ($CDCl_3$) τ −2.48 (m, 14.5 H, aromatic, plus 0.5 PH), 6.35 (s, 0.5 H, 0.5 PH); ^{31}P NMR ($CDCl_3$) σ 39.9 (d, J = 193 Hz). Anal. ($C_{20}H_{15}P$) C, H, P.

Bis(α,α,α-trifluoro-3-tolyl)phosphine. Diphenylsilane reduction[26] of the phosphine oxide gave an 89% yield of the phosphine: bp 71–75 °C (0.4 mm); ^1H NMR ($CDCl_3$) τ ~2.43 (m, 8 H, aromatic), 4.74 (d, 1 H, J = 217 Hz, PH).

(*R,R*)-*trans*-4,5-Bis[[bis(1-naphthalenyl)phosphino]-methyl]-2,2-dimethyl-1,3-dioxolane (1b). A slurry of lithium bis(1-naphthalenyl)phosphide was prepared by addition of 0.036 mol of *n*-butyllithium in hexane to 10.3 g (0.036 mol) of bis(1-naphthalenyl)phosphine in 50 mL of benzene. To this mixture was added dropwise a solution of 8.46 g (0.018 mol) of (−)-2,3-*O*-isopropylidene-1,4-di-*p*-tosylbutane in 60 mL of tetrahydrofuran. The mixture was allowed to react an additional 1.5 h, the solvent was evaporated, and the residue taken up in water and benzene. The benzene solution was dried over $MgSO_4$ and filtered, and the benzene was evaporated under vacuum. The residue was extracted with ether, leaving 0.33 g of insoluble tetrakis(1-naphthalenyl)biphosphine: mp 252–258 °C; ^{31}P NMR ($CDCl_3$) δ 39.27. Anal. Calculated for $C_{40}H_{28}P_2$: C, 84.20; H, 4.95; P, 10.86; mol wt 570. Found: C, 83.70; H, 5.02; P, 11.02; mol wt 544 (C_6H_6).

The ether extract was diluted with cyclohexane and slowly deposited crystals of (*R,R*)-*trans*-4,5-bis[[bis(1-naphthalenyl)-phosphino)methyl]-2,2-dimethyl-1,3-dioxolane–cyclohexane solvate: 8.4 g (67%); mp 104–106 °C; $[\alpha]^{20}_D$ −0.46° (*c* 2.2, C_6H_6);

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^{1}H NMR ($CDCl_3$) τ 2.33 (m, 28 H, aromatic), 6.02 (q, 2 H, HCO), 7.53 (m, 4 H, PCH_2), 8.60 (s, 12 H, cyclohexane), 8.73 (s, 6 H, CH_3); ^{31}P NMR ($CDCl_3$) δ 46.79. Anal. ($C_{53}H_{52}OP$), C, H, P.

(*R,R*)-*trans*-4,5-Bis[[bis(2-naphthalenyl)phosphino]-methyl]-2,2-dimethyl-1,3-dioxolane (1c). Reaction of the lithium salt of bis(2-naphthalenyl)phosphine with (-)-2,3-*O*-isopropylidene-1,4-di-*p*-tosylbutane was carried out as described above for the 1-naphthalenyl analogue. The product had the following: mp 110–125 °C (EtOH–C_6H_6); $[\alpha]^{20}_D$ +13.91° (*c* 2.0, C_6H_6); ^{1}H NMR ($CDCl_3$) τ 2.4 (m, 28 H, aromatic), 5.92 (q, 2 H, HCO), 7.37 (d, 4 H, PCH_2), 8.62 (s, 6 H, CH_3); ^{31}P NMR ($CDCl_3$) δ 22.58. Anal. ($C_{47}H_{40}O_2P_2$) C, H, P.

(*R,R*)-*trans*-4,5-Bis[(2,8-dimethylphenoxaphosphino)-methyl]-2,2-dimethyl-1,3-dioxolane (1f). A solution of 2.28 g (0.010 mol) of 2,8-dimethylphenoxaphosphine[26] in 15 mL of dry tetrahydrofuran was treated with a total of 0.40 g (0.010 mol) of dry potassium hydride added in small portions under a dry nitrogen atmosphere. To the resulting orange-red solution was added 2.3 g (4.9 mol) of (-)-2,3-*O*-isopropylidene-1,4-di-*p*-tosylbutane in 10 mL of tetrahydrofuran, and the mixture was stirred for 12 h. The solvent was evaporated at reduced pressure, and the residue was taken up in water and ether. The ether layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated under reduced pressure to yield a tan solid: $[\alpha]^{20}_D$ -43.1° (*c* 1.0, toluene); ^{1}H NMR ($CDCl_3$) τ ~2.85 (m, 12.6 H, aromatic), 6.55 (q, 2.6 H, HCO), 7.71 (s, 12.7 H, aryl CH_3), 8.37 (d, 3.2 H, PCH_2), 8.68 (s, 4.9 H, isopropyl CH_3); ^{31}P NMR ($CDCl_3$) δ 67.12 (90%), impurities at δ 15.74 and -4.67. Attempts to recrystallize the material from various solvents were unsuccessful. Anal. Calcd for $C_{35}H_{36}O_4P_2$: C, 72.15; H, 6.22; P, 10.63. Found: C, 69.81; H, 6.45; 10.50.

(*R,R*)-*trans*-4,5-Bis[[bis(α,α,α-trifluoro-3-tolyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (1d). Reaction of the potassium salt of bis(α,α,α-trifluoro-3-tolyl)phosphine with (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-di-*p*-tolylbutane in the manner described above for the phenoxaphosphine analogue afforded the expected compound as an oil: $[\alpha]^{20}_D$ +3.24° (*c* 1.0, toluene); ^{1}H NMR ($CDCl_3$) τ ~2.4 (m, 16 H, aromatic), 6.00 (m, 2 H, HCO), 7.57 (m, 4 H, PCH_2), 8.69 (s, 6 H, CH_3); ^{31}P NMR ($CDCl_3$) δ 20.07.

(-)-*trans*-4,5-Bis[(*p*-tosyloxy)methyl]-2,2-diphenyl-1,3-dioxolane. A mixture of 4.3 g (0.01 mol) of (-)-1,2,3,4-butanetetrol 1,4-ditosylate,[30] 2.4 g (0.01 mol) of dichlorodiphenylmethane, and 25 mL of *o*-dichlorobenzene was heated to reflux under nitrogen with HCl gas evolution for 12 h. Solvent was evaporated at reduced pressure giving a solid residue which was recrystallized from C_6H_6–heptane to yield 3.6 g (60.5%) of product: mp 121–122 °C; $[\alpha]^{20}_D$ -6.36° (*c* 1.0, C_6H_6); ^{1}H NMR (acetone-d_6) τ 2.43 (m) and 2.74 (m) (18 H total, aromatic), 5.84 (m, 6 H, HCO), 7.54 (s, 6 H, tosyl CH_3). Anal. Calcd for $C_{31}H_{30}O_8S_2$: C, 62.61; H, 5.09; S, 10.78. Found: C, 63.00; H, 5.20; S, 10.26.

(*R,R*)-*trans*-4,5-Bis[(diphenylphosphino)methyl]-2,2-diphenyl-1,3-dioxolane (2). A solution of 12.8 mmol of lithium diphenylphosphide in 40 mL of tetrahydrofuran was prepared from diphenylphosphine and lithium wire, and 2-chloropropane was used to destroy the phenyllithium formed.[31] To this solution was added 3.6 g (6.05 mmol) of (-)-*trans*-4,5-bis[(*p*-tosyloxy)-methyl]-2,2-diphenyl-1,3-dioxolane in 25 mL of tetrahydrofuran, and the mixture was allowed to stir overnight. Evaporation of the solvent followed by hydrolysis of the residue with water, extraction with benzene, and evaporation of the benzene under reduced pressure afforded a dark syrup which was triturated with ethanol to yield solid product: mp 135–137 °C (EtOH–C_6H_6); $[\alpha]^{20}_D$ -40.4° (*c* 1.0, C_6H_6); ^{1}H NMR (C_6D_6) τ 2.73 (m, 30 H, aromatic), 5.90 (m, 2 H, HCO), 7.58 (m, 4 H, CH_2P). Anal. ($C_{41}H_{36}O_2P_2$) C, H, P.

Hydroformylation Runs. Reactions were carried out in benzene solvent unless otherwise noted; the concentrations of rhodium compound and vinyl esters were 8×10^{-4} and 3.45 M, respectively, for all runs. A 44:56 CO/H_2 mixture was used. Catalyst, ligand, solvent, and vinyl esters were charged to the reactor which was then purged with the CO/H_2 gas mixture, and the contents were heated to the desired temperature under 100 psig of gas. The gas pressure was then set at the desired level, and reactions were carried out with vigorous shaking at constant pressure, with a calibrated reservoir to feed gas as consumed. Generally, reactions were carried to completion or until gas uptake ceased. Average rates were calculated on total gas uptake over the period of the run. Reaction mixtures were analyzed by gas chromatography using a Hewlett-Packard 7620 gas chromatograph and a 2 m × $^1/_4$ in o.d. glass column with Tenax GC packing, temperature programmed from 125 to 250 °C at 10 °C/min. Experimental conditions along with yield and rate data are summarized in Tables I and II.

Determination of Enantiomeric Excess. 2-Acetoxypropanal. Optical rotation for the pure material was determined in two ways. A sample of aldehyde, obtained by distillation from several runs and having a $[\alpha]^{20}_D$ of -13.08° (*c* 5.0, toluene), was oxidized in benzene solution with oxygen at 60 psig and room temperature for 24 h to afford (*S*)-2-acetoxypropionic acid, $[\alpha]^{20}_D$ -18.48° (*c* 7.2, $CHCl_3$) [lit.[32] $[\alpha]^{20}_D$ -49.3° (*c* 7.2, $CHCl_3$) for pure *S*-(-) acid]. On the assumption of the same enantiomeric excess, 37.5%, for the aldehyde and the acid, the calculated rotation for the pure aldehyde is $[\alpha]_D$ -34.9° (*c* 5.0, toluene). The enantiomeric excess was also determined on the aldehyde directly by integration of the NMR spectrum obtained in the presence of tris[3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato]europium.[33,34] Optical rotation for the pure aldehyde was calculated to be $[\alpha]^{20}_D$ -35.1° (*c* 5.0, toluene), in good agreement with the value determined by oxidation to the acid.

The enantiomeric excess for each hydroformylation run was determined either on the aldehyde isolated by distillation from the reaction mixture or on the reaction mixture itself. A correlation was established between rotation of the isolated aldehyde in toluene and that of the reaction mixture in benzene. The enantiomeric excess was then calculated by using the formula:

$$\% \text{ ee} = 10^4\alpha/c(3000 + 21c) \quad (2)$$

where α is rotation of the reaction mixture and c is the percent concentration of 2-acetoxypropanal in the reaction mixture, as determined by GLC. Periodic checks of the two methods gave agreement to ±1% for the same run. Results are summarized in Table I.

2-Propionoxypropanal. A 5-g sample of 2-propionoxypropanal [bp 73–78 °C (32 mm), $[\alpha]^{20}_D$ +9.04° (*c* 5.0, toluene)] isolated from hydroformylation of vinyl propionate was dissolved in 10 mL of C_6H_6, 0.1 g each of cupric oxide and silver oxide were added, and the mixture was placed under 75 psig of oxygen for 48 h. Metals were precipitated by adding concentrated aqueous Na_2CO_3. The mixture was filtered and extracted with ether, and the filtrate was acidified in the cold with concentrated HCl. The mixture was extracted with ether and the ether extract distilled to yield 2-propionoxypropionic acid: bp 83–85 °C (0.4 mm); $[\alpha]^{20}_D$ +16.18° (*c* 5.0, $CHCl_3$). A reference sample of (*S*)-(-)-2-propionoxypropionic acid, prepared by esterification of (*S*)-(+)-lactic acid with propionic acid with Dowex 50W exchange resin had $[\alpha]^{20}_D$ -64.16° (*c* 5.0, $CHCl_3$). The ee of the sample of acid prepared by oxidation of the aldehyde was thus 25.2%, and on the assumption of the same ee for the aldehyde the calculated rotation for pure (*R*)-(+)-2-propionoxypropanal is $[\alpha]^{20}_D$ +35.9° (*c* 5.0, toluene). Enantiomeric excess for each hydroformylation run was determined on a sample of aldehyde isolated by distillation from the reaction mixture. Results are summarized in Table II.

2-(Benzoyloxy)propanal. A sample of aldehyde isolated from asymmetric hydroformylation runs had the following: bp 82–85 °C (20 mm); ^{1}H NMR (270 MHz, $CDCl_3$) τ 0.32 (s, 1 H, CH=O), 1.89 (2 d, 2 H, *o*-aryl), 2.38 (Et, 1 H, *p*-aryl) 2.51 (t, 2 H, *m*-aryl), 4.68 (q, 1 H, HCO), 8.44 (d, 3 H, CH_3). Addition of tris[3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato]europium caused doubling of all peaks; the enantiomeric excess determined

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from the ratios of peak pair integrals at τ 0.29 and 0.35 (17.2-Hz separation) and at τ 1.08 and 1.21 Hz (*o*-aryl, 34.1-Hz separation) was 30% ee.[35] Since the aldehyde sample had $[\alpha]^{20}_D$ −9.24° (*c* 4.5, C_6H_6), the rotation for the enantiomerically pure aldehyde is $[\alpha]^{20}_D$ −30.8 ± 1° (*c* 4.5, C_6H_6). Asymmetric hydroformylation results are summarized in Table II.

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(35) We thank Professor W. H. Urry, University of Chicago, for this determination.

Registry No. (*R,R*)-**1a**, 32305-98-9; (*S,S*)-**1a**, 37002-48-5; (*R,R*)-**1b**, 78870-98-1; (*R,R*)-**1c**, 78890-48-9; (*R,R*)-**1d**, 78870-99-2; (*R,R*)-**1e**, 57221-96-2; (*R,R*)-**1f**, 78871-00-8; (*R,R*)-**2**, 78871-01-9; vinyl propionate, 105-38-4; vinyl benzoate, 769-78-8; (*R*)-2-propionoxypropanal, 78871-02-0; (*S*)-2-propionoxypropanal, 78871-03-1; (*R*)-2-(benzoyloxy)propanal, 78871-04-2; Rh(1,5-COD)[(*S,S*)-*trans*-4,5-bis[5*H*-dibenzophospholyl)methyl]-2,2-dimethyl-1,3-dioxolane] perchlorate, 60594-33-4; bis(1-naphthalenyl)phosphine oxide, 13440-07-8; bis(2-naphthalenyl)phosphine oxide, 78871-05-3; bis(α,α,α-trifluorotolyl)-phosphine oxide, 15929-44-9; bis(1-naphthalenyl)phosphine, 39864-75-0; bis(2-naphthalenyl)phosphine, 78871-06-4; bis(α,α,α-trifluoro-3-tolyl)phosphine, 65796-64-7; tetrakis(1-naphthalenyl)biphosphine, 78890-49-0; (−)-*trans*-4,5-bis[(*p*-tosyloxy)methyl]-2,2-diphenyl-1,3-dioxolane, 78871-07-5; (*S*)-2-acetoxypropanal, 66875-70-5; (*S*)-2-acetoxypropionic acid, 6034-46-4.

Generalization of the Triptycene Concept. Use of Diaryne Equivalents in the Synthesis of Iptycenes

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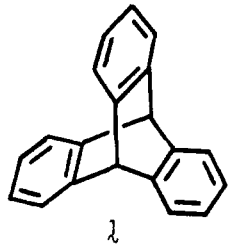
A simple one-step synthesis of triptycene analogues prepared by reaction of a diaryne equivalent with anthracenes is described. For example, 1,2,4,5-tetrabromobenzene, anthracene, and *n*-butyllithium gave 5,7,12,14-tetrahydro-5,14[1′,2′]:7,12[1″,2″]-dibenzenopentacene (**2**, R = H; trivially called a *p*-pentiptycene) in good yield. Other tetrabromoarenes were used to similarly prepare **2** (R = CH_3), **2** (R = OCH_3), and the naphtho analogue **13**. Use of 9,10-dimethoxyanthracene gave the tetramethoxy bridgehead-substituted pentiptycene **11**. 4,5-Dibromo-3,6-diiodo-*o*-xylene functioned as an ortho diaryne equivalent to give the *o*-pentiptycene **3** (R = CH_3). The synthesis of heptiptycene **4** (5,6,11,12,17,18-hexahydro-5,18[1′,2′]:6,11[1″,2″]:12,17[1‴,2‴]-tribenzenotrinaphthylene has been improved, and the intermediate cycloalkyne **22** has been trapped with various dienes.

Bartlett[1] was the first to synthesize triptycene (**1**), for



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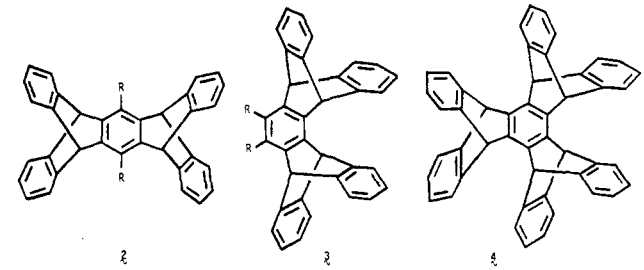
the purpose of testing certain concepts in physical-organic chemistry. For example, bridgehead-substituted triptycenes were used to generate the corresponding carbonium ions, radicals, and carbanions, and these were compared with their trityl analogues.[2] Interest in triptycene rose sharply when it was shown by Wittig that it could be synthesized easily in one step from benzyne and anthracene,[3] and at one point the formation of triptycene actually became a test for the efficacy of various benzyne precursors.[4] Eventually, the synthesis of triptycene became a standard undergraduate laboratory "experiment".[5]

Many substituted triptycenes are known, and the benzene rings have also been replaced with a variety of other aromatic rings.[6] The rigid framework is attractive and has been used to study such diverse phenomena as intramolecular charge transfer[7] and restricted rotation about single bonds.[8] In the many structural variations on triptycene, the triptych or triplanar nature of the structures has been preserved.[9]

If triptycene is viewed *not* as a benzyne derivative of anthracene but rather as a benzene which is ortho-disubstituted by attachment to the 9,10-positions of anthracene, then one quickly observes that this concept might be extended by connection to two or three anthracenes as shown in **2**–**4**. We propose that these substances be given the trivial name of "iptycenes".[11,12]



2 **3** **4**

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