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Homogeneous Hydrogenation of Substituted (Z) - Ene-1,2-Dicarbamates with Rh(I) Phosphine Complexes

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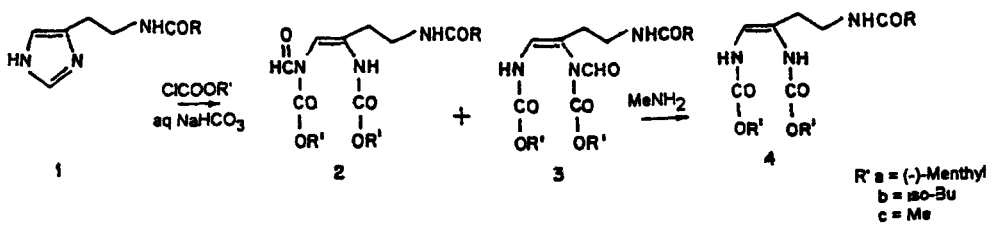
Abstract: *Homogeneous hydrogenation of substituted (Z)-ene-1,2-di-(-)-(1R, 3R, 4S)-menthylcarbamate catalysed by rhodium complexes containing (+)-(2S,3S) or (-)-(2R,3R)-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) gives rise to the saturated products with a diastereomeric excess (de) of 47% and 40%, respectively Hydrogenation of substituted (Z)-ene-1,2-di-iso-butylcarbamate affords an enantiomeric excess (ee) of 20% and 18%*

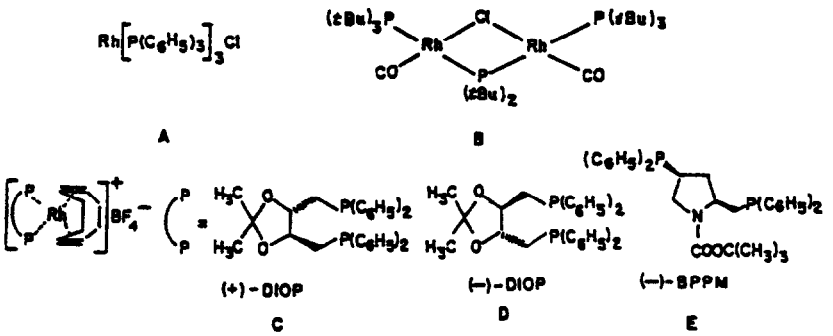
Most studies of homogeneous enantioselective hydrogenation using Rh or Ru complexes as catalysts have been performed with N-acylamino unsaturated acids, dehydropeptides, ketones[1] and imines[2] The homogeneous hydrogenation of substituted (*Z*)-ene-1,2-dicarbamates had not previously been investigated Ene-1,2-dicarbamates are obtained upon Bamberger-ring cleavage acylation of imidazoles[3] Their hydrogenation with Pd or Raney Ni, followed by removal of acyl groups, is an approach to the synthesis of vicinal diamines having an additional function[4], or of selectively protected 1,2,4-triaminobutanes[5] These compounds are important in chelation chemistry[5], as intermediates in the synthesis of ligands used for radiolabelling and imaging[6] and in synthesis of heteromacrocycles[7] The question arises whether homogeneous hydrogenation, using Rh(I) complexes as catalysts would lead to enantioselective synthesis

4a has been chosen as the substrate for hydrogenation studies It is easily prepared from N^{in}-anisoyl histamine **1.** The anisoyl group has a characteristic UV absorption which can be useful in following the synthetic steps on TLC The open-chain ene-dicarbamate **4a** was obtained with (-)-(1*R*, 3*R*, 4*S*)-menthyl chloroformate[8] as acylating reagent under Schotten Baumann reaction conditions, followed by removal of the formyl group (Scheme 1)

Scheme 1



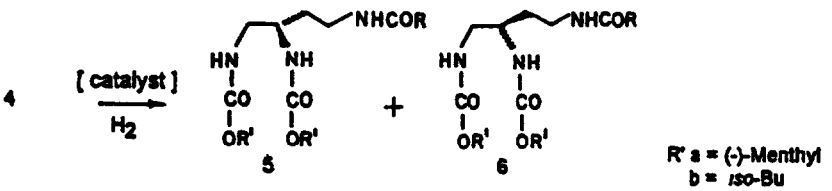
Homogeneous hydrogenation of **4a** was performed with neutral non-chiral complexes viz, $[Rh(I)(Ph)_3P]_3Cl$ **A**[9], binuclear Rh(I) carbonyl compound **B**[10], and with ionic complexes[11,12] having chiral phosphine ligands[13,14] viz, $[Rh(+)DIOP(COD)]^+BF_4^-$ **C**, $[Rh(-)DIOP(COD)]^+BF_4^-$ **D** and $[Rh(-)BPPM(COD)]^+BF_4^-$ **E** Hydrogenation was carried under 650 psi of hydrogen at 20-50°C in ethanol-benzene (3 7) (Table 1) All catalysts afforded mixtures of diastereomers **5a** and **6a**, **5a** having the configuration *R* at the newly formed diastereocenter and **6b** having the configuration *S* (Scheme 2)



A B C D E

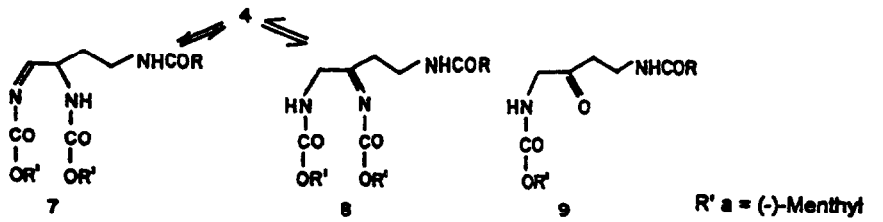
The non-chiral substrate **4b** was hydrogenated only with the catalysts **C** and **D** The lowest homologue **4c** (R' = Me), due to its low solubility, was unsuitable for hydrogenation studies It could be reduced under heterogeneous conditions with 10% Pd on charcoal or with Raney nickel in ethanol

Scheme 2



The two (-)-menthyl groups influence the course of homogeneous hydrogenation of **4a** with neutral non-chiral complexes **A** and **B**, inducing low diastereomeric excess (de) of 23% and 26% respectively, both with the configuration *R* of the major component **5a** Conversion did not exceed 50% at 50°C When hydrogenation was performed at 70°C, ketone **9a** was isolated in addition to **5a** and **6a**, probably owing to isomerization of **4a** to the unstable acyl-imine **8a**, which upon workup underwent hydrolysis Induction was not observed under heterogeneous hydrogenation conditions using 10% Pd-C or Raney Ni

Scheme 3



Using ionic Rh(I) complexes **C** and **D** containing chiral biphosphine ligands (+)DIOP and (-)DIOP in hydrogenation of **4a**, a moderate de of 40% (*R*) and 47% (*S*) respectively was obtained, as measured by ^{1}H NMR spectra The configuration of the major component was dependent on the stereochemistry of the chiral ligand of the catalyst (see Table 1) The assignment of the absolute configuration was based on comparison with the compound prepared by unambiguous synthesis, starting from (S)-pyroglutamic acid methyl ester, *via* chiral 4,5-diaminovaleric acid[15], which was subjected to the Curtius reaction and acylations[16] The complex [Rh(-)BPPM (COD)]$^+$ **E** appeared to be ineffective in hydrogenation of **4a** The enantiomeric excess (ee) obtained upon hydrogenation of the non-chiral substrate **4b** (R = *iso*-Bu) with the catalyst **C** was 20% (*R*) and with the catalyst **D** 18% (*S*) The optical yield was calculated on the basis of the value for the optically pure compound prepared by unambiguous synthesis, which was $[\alpha]_D^{25}$ - 37 2 (c 3 6, EtOH)[16]

Table 1 Hydrogenation of N^1,N^2-Dialkoxycarbonyl-N^4-anisoyl-1,3,4-triaminobut-1-enes with Rh(I) Phosphine Complexes

Substrate	Catalyst	t°C	Conversion %	Ratio of **5** **6**	Optical yield*
4a	A	50	60	62 38	24 *R*
4a	B	50	50	63 37	26 *R*
4a	C	20	100	70 30	40 *R*
4a	C	50	100	74 26	48 *R*
4a	D	20	60	30 70	40 *S*
4a	E	20	100	50 50	0
4b	C	20	50	60 40	20 *R*
4b	D	30	40	41 59	18 *S*

Reaction conditions substrate 0 25 mMol, [Rh] 3x10^{-2} mMol, benzene-ethanol 7 3, 10mL, pressure 650 psi, reaction time 72 h , *ed - in the case of hydrogenation of **4a**, was measured by 1H-NMR; ee - in the case of **4b**, was measured by optical rotation with respect to the optically pure compound (2*S*)-N^1,N^2-di*iso*butyloxycarbonyl-N^4-anisoyl-1,2,4-triaminobutane[16]

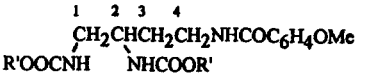
5a and **6a** differ in the chemical shifts of the butane skeleton carbons in ^{13}C NMR spectra (see Table 2) and in the chemical shifts of NH protons **5a** shows a triplet at 4 91 ppm of NH-1 and a doublet at 5 36 ppm of NH-2 whereas the corresponding NH triplet of **6a** appears at 4 99 ppm and the doublet at 5 43 ppm, the ratio of the two doublets and the two triplets was determined by integration

The two carbamate substituents, whether containing the bulky (-)menthyl group (**5a**, **6a**) or the small alkyl group, such as Me (**5c**,**6c**), impose hindered rotation on the molecule at room temperature[17], giving a broad pattern of protons bound to the stereogenic center at C-2 and to prochiral positions at C-1, C-3 and C-4 ^{1}H chemical shift assignments could be obtained only with ^{1}H-^{13}C correlated spectra

The mechanism of hydrogenation of substituted (Z)-ene-1,2-dicarbamates is not clear and imposes several questions Does a molecule of the catalyst have an equal chance to be coordinated by each of the carbamates or is the coordination to that at C-1, which is the less hindered of the two, preferred? Equal chances would lead to a racemic product and this may be the case with [Rh(-)BPPM]$^+$ **E** as a catalyst The second question is whether hydrogenation proceeds by reduction of the C=C double bond, or whether isomerization to acyl-imines **7** and **8** takes place upon complexation, following the C=N double bond reduction.

Tautomerization to **7**, prior to hydrogenation, would also give rise to a racemic mixture Isolation of ketone **9** from hydrogenation experiments performed with catalyst **A** or with catalyst **B** does not rule out the possibility that tautomerization did indeed take place at 70-90°C, but the intermediate acyl-imine **8** withstood reduction, undergoing hydrolysis during workup procedure

Table 2 Selective Data for ^1H and ^{13}C Chemical Shifts for N^1,N^2-Dialkoxycarbonyl-N^4-anisoyl-1,2,4-triaminobutanes **5** and **6**



Compound	H-1	H-2	H-3	H-4	NH-1	NH-2	NH-4	C-1	C-2	C-3	C-4	R'
5a[a]	2 9-3 3	3 7	1 4 1 7	2 9 3 7	4 91	5 36	7 59	44 5	50 3	33 0	35 6	C-1' 31 4, C-2' 41 2, 41 3, C-3' 75 0, 75 2, C-4' 47 2, C-5' 23 4, 23 5, C-6' 34 2, C-7' 22 0, C-8' 26 1, 26 2, C-9' 20 7, 20 8, C-10' 16 4
6a[a]	3 1 -3 3	3 7	1 5 1 7	3 0 3 8	4 99	5 43	7 45	45 0	49 6	32 9	36 1	
5b, 6b[a]	3 1-3 3	3 7	1 5 1 8	3 2 3 8	5 34	5 63	7 48	44 8	50 2	32 7	36 0	CH_3 18 9, CH 27 9, CH_2O 71 3
5c, 6c[b]	3 1-3 3	3 7	1 5 1 7	3 1 3 7	6 79	6 81	7 58	44 0 44 1	49 2	29 5	35 4 35 5	CH_3O 51 0, 51 1

[a] measured in $CDCl_3$, [b] measured in a mixture acetone-d_6 - $CDCl_3$

EXPERIMENTAL

Melting points were uncorrected. Infrared spectra were recorded on a Perkin Elmer 257 spectrophotometer ^1H and ^{13}C NMR spectra were measured on a AM Bruker 400 MHz WB spectrometer Mass spectra were obtained on a TSQ-70 mass spectrometer and on varian MAT 711 double focusing mass spectrometer Specific rotation was measured with a DIP JASCO polarimeter Elemental analyses were performed by Microanalytical Services of the Chemistry Department at the Hebrew University of Jerusalem. TLC was performed on Merck silica gel 60 F_{256} (+)DIOP and (-)DIOP were obtained from Strem Chemicals Inc and (-)-BPPM from Aldrich

N^w-Anisoylhistamine (1). The solution of N-hydroxysuccinimide ester, prepared by consecutive addition of anisic acid (456 mg, 3 mmol), N-hydroxy succinimide (366 mg, 3 3mmol) and dicyclohexylcarbondiimide (680 mg, 3 4 mmol) into dry DMF (20 mL) at -10°C, was slowly added into a solution of histamine, prepared by neutralization of histamine dihydrochloride (552 mg, 3 mmol) with Et_3N (606 mg, 6mmol), in dry DMF (40 mL) at -10°C The mixture was stirred for 1 h at -10° and left at room temperature for two days. DMF was removed in vacuo The residue was mixed with EtOAc (30 mL) and HCl 2M (30 mL) and separated from dicyclohexylurea at the interface by filtration The aqueous layer was separeted, extracted once more with EtOAc (10 mL), brought to pH 10 with 10M KOH and extracted 5 times with EtOAc The extract was dried (Na_2SO_4) and concentrated, giving 650 mg (88%) of **1** mp 158-159° (needles from water), Rf 0 22 ($CHCl_3$ EtOH Et_3N - 7 8 2 0 2), visualization with Pauly reagent[18], IR (KBr) 1630, 1608, 1560 cm-1, ^1H NMR (DMSO-d_6) 2 72 (t, 2H, CH_2), 3 42 (m, 2H, CH_2), 3 78 (s, 3H, CH_3), 6 79 (s, 1H, Im-5), 6 97 (d, 2H, arom) 7 52 (s, 1H, Im-2), 7 80 (d, 2H, Im-2), 8 43 (t, 1H, NH), HRMS 246 1236 $[MH]^+$ (7 2%), 245 1176 M^+ (38%), 135 4449 $[O{=}C\text{-}C_6H_4OCH_3]^+$ (100%) Anal found C, 63 78, H, 5 98, N, 16 94 $C_{13}H_{15}N_3O_2$ requires C, 63 65, H, 6 16, N, 17 13%.

N^1 and N^2-formyl-N^1,N^2di(-)menthyloxycarbonyl-N^4-anisoyl-1,2,4-triaminobut-1-ene (2a,3a). (-)-Menthyl chloroformate (972 mg, 8mmol) in EtOAc (20 mL) and $NaHCO_3$ (700 mg) in water (20 mL) were simultaneously added, from two separate funnels, into a suspension of **1** (490 mg, 1mmol) in EtOAc (40 mL) and water (10mL) which was kept in an ice-bath. The mixture was stirred for 1h at 0°C and overnight at room temperature The organic layer was separated, dried, concentrated and put, in a minimum volume of EtOAc, onto a silica gel column (40 g) prepared in hexane Menthol and dimenthyl carbonate were

eluted with 10% EtOAc-hexane Elution with 20% EtOAc-hexane gave the product **2a,3a**. 1 24 g, (98%), mp 101 - 104°, Rf 0 80 (60% EtOAc-hexane, visualization with UV and I_2), IR ($CHCl_3$) 1730, 1700, 1645, 1605 cm, ^1H NMR ($CDCl_3$ 6 52 and 6 65 (C=CH), 7 1 (*NH*), 8 2-8 4 (NH), 9 18 and 9 28 (CH=0), CIMS *m/z* 628 3 $[MH]^+$ (100%), Anal Found. C, 67 04, H, 8 34, N, 6 87 $C_{35}H_{53}N_3O_7$ requires C, 66 96, H, 8 57, N, 6 87%.

***N*¹,*N*²-Di(-)menthyloxycarbonyl-*N*⁴-anisoyl-1,2,4-triaminobut-1-ene (4a).** Deformylation was carried out by treating **2a, 3a** (272 mg) in ether (5 mL) with 11% $MeNH_2$ in ether (5mL) at room temperature for 12 h The solution was washed with water, dried and concentrated, yielding quantitatively **4a**, mp 83 - 85°, Rf 0 72 (60% EtOAc-hexane), IR ($CDCl_3$) 1700, 1644, 1605 cm^{-1}, ^1H NMR ($CDCl_3$) 0 86 - 2 00 (m, 36H, (-)-menthyl + CH_2), 2 34 (t, 2H, CH_2), 3 49 (q, 2H, CH_2N), 3 78 (s, 3H, 0Me), 4 57 (s, 3H, 0CH), 6 22 (d, 1H, C=CH), 6 42 (s, 1H, NH), 6 72 (br, 1H, NH), 6 85 (d, 2H, arom), 7 20 (br, 1H, NH), 7 70 (d, 2H, arom), CIMS *m/z* 600 $[MH]^+$ (100%), Anal Found C, 68 08, H, 8 75, N, 7 01 $C_{34}H_{53}N_3O_6$ requires C,68 08, H,8 90, N, 7 00%.

***N*¹,*N*²-Di-*iso*-butoxycarbonyl-*N*⁴-anisoyl-1,2,4-triaminobut-1-ene (4b).** Ring cleavage of 1 with *iso*-butyl chloroformate and deformylation, as described above, yielded **4b** in 83%, mp 125 - 127°, IR ($CHCl_3$) 1720, 1700, 1603 cm^{-1}, ^1H NMR ($CDCl_3$) 0 86 (d, 6H, Me), 0 89 (d, 6H, Me), 1 90 (q, 2H, CH), 2 35 (t, 2H, CH_2), 3 50 (q, 2H, CH_2N), 3 79 (s, 3H, OMe), 3 84 (d, 4H, OCH_2), 6 25 (d, 1H, C=CH), 6 58 (d, 1H, NH), 6 85 (d, 2H, arom), 6 21 (br, 1H, NH), 7 68 (d, 2H, arom), CIMS *m/z* 436 $[MH]^+$ (100%), Anal Found C, 60 90, H, 7 54, N, 9 73 $C_{22}H_{33}N_3O_6$ requires C, 60 67, H, 7 63, N, 9 64%

***N*¹,*N*²-Dimethoxycarbonyl-*N*⁴-anisoyl-1,2,4-triaminobut-1-ene (4c).** 4c was prepared as described above **2c** and **3c** were eluted from a silica gel column using EtOAc-hexane 1 1 together with some deformylated product. Deformylation was completed by treating the mixture with methanol at room temperature for 72 h. Mp 198°C, IR (KBr) 1725, 1715, 1618, 1603 cm^{-1}, ^1H NMR ([D_6]DMSO) 2 4 - 2 6 (m, 2H, CH_2), 3 26 (m, 2H, CH_2N), 3 56 (s, 3H, OCH_3) , 3 58 (s, 3H, OCH_3), 3 76 (s, 3H, OCH_3), 5 94 (d, 1H, C=CH), 6 97 (d, 2H, arom), 7 77 (d, 2H, arom), 8 11 (br, 1H, NH), 8 23 (t, 1H, NH), 8 71 (d, 1H, NH), CIMS *m/z* 354 $[MH]^+$ (100%), Anal Found C, 54 40, H, 5 77, N, 11 59 $C_{16}H_{21}N_3O_6$ requires C, 54 69, H, 6 02, N, 11 95%.

Homogeneous Hydrogenation

General method The catalysts containing chiral bis(tertiaryphosphine) ligands were prepared by Glaser's modification[12] of Schrock and Osborn's[11] method The catalyst ($3x10^{-2}$ mmol) was dissolved in degassed absolute ethanol (3 mL), mixed with **4a** or **4b** (0 25 mmol) in degassed dry benzene (7 mL) Hydrogenation was carried out in an autoclave for 72 h at a hydrogen pressure of 650 psi Solvent was evaporated and the residue purified on preparative 2mm silica gel TLC 20x20 cm, eluted with EtOAc-hexane 6 4 or by flash chromatography on silica gel column. The fraction containing the reduced product was analysed by ^1H and ^{13}C NMR spectra or by polarimeter Hydrogenation with non-chiral catalysts **A** and **B**[10] was performed by the same procedure

***N*¹,*N*²-Di-(-)menthyloxycarbonyl-*N*⁴-anisoyl-1,2,4-triaminobutane (5a,6a)** obtained from hydrogenation, using [Rh(+)-(DIOP)]$^+$ as catalyst (see Table 1) had mp 187-191°C, IR ($CHCl_3$) 1696, 1644, 1605 cm^{-1} , CIMS *m/z* 602 $[MH]^+$ (100%), Anal Found C, 67 63, H, 8 96, N, 6 76 $C_{34}H_{55}N_3O_6$ requires C, 67 85, H, 9 21, N, 6 98%. A double crystallization from ethanol gave **5a**, still contaminated by a small amount of **6a** which cannot be evaluated by ^1H NMR., mp 191-193°C For ^1H and ^{13}C NMR data see Table 2 **5a,6a** from hydrogenation using [Rh(-)(DIOP)]$^+$ as catalyst had mp 186-190°C, IR ($CHCl_3$) 1698, 1646, 1604 cm^{-1} A double crystallization from benzene gave **6a** contaminated with some **5a**, mp 190-194°C For ^1H and ^{13}C NMR data see Table 2

***N*¹-Menthyloxycarbonyl-*N*⁴-anisoyl-1,4-diamino-2-butanone (9).** The reaction mixture from hydrogenation with catalyst **A** at 90°C was concentrated and applied onto a silica gel column (15 g) prepared in hexane (-)-Menthyl carbamate (31mg) was eluted with 10% EtOAc-hexane, **5a,6a** were obtained with 20% EtOAc-hexane (27 mg, 17%) Elution with 40% EtOAc yielded ketone 9 73 mg (70%), mp 126°C, IR ($CHCl_3$) 1704, 1650, 1602 cm^{-1}, ^1H NMR ($CDCl_3$) 0 7-2 0 (m, 18H, menthyl), 2 65 (t, 2H, CH_2CO), 3 70 (q, 2H, CH_2N), 3 81 (s, 3H, CH_3O), 4 02 (d, 2H, CH_2N), 4 55 (m, 1H, CHO), 5 30 (t, 1H, NH-1), 6 24 (t, 1H, NH-4), 6 90 (d, 2H, arom), 7 75 (d, 2H, arom) , CIMS *m/z* 419 $[MH]^+$ (100%), Anal Found C, 66 19, H, 8 18, N, 6 70 $C_{23}H_{34}N_2O_5$ requires C, 66 00, H, 8 18, N, 6 69% When the hydrogenation reaction was carried out with the catalyst **B** at 70°C **5a,6a** was obtained with a 52% and **9** with a 34% yield

***N*¹,*N*²-Di-*iso*-butoxycarbonyl-*N*⁴-anisoyl-1,3,4-triaminobutane (5b,6b).** The hydrogenation of **4b** using [Rh(+)(DIOP)]$^+$ gave **5b,6b** (50%) yield and the recovered olefin (50%) **5b,6b** had mp 117°C, $[\alpha]_D^{25} = +7\ 4$ (c 1 7, EtOH), IR ($CHCl_3$) 1700, 1644, 1604 cm^{-1}, for ^1H and ^{13}C NMR data - see Table 2, CIMS *m/z* 438 $[MH]^+$ (100%), Anal Found C, 60 20, H, 8 02, N, 9 33 $C_{22}H_{35}N_3O_6$ requires C, 60 39, H, 8 06, N, 9 60%. The hydrogenation of **4b** in the presence of [Rh(-)(DIOP)]+ gave the mixture of **5b,6b** having mp 114-116°, $[\alpha]_D25 = -6\ 6$ (c 2, EtOH)

***N*¹,*N*²-Dimethoxycarbonyl-*N*⁴-anisoyl-1,2,4-triaminobutane (5c,6c).** Substrate **4c** (200mg) in ethanol (50 mL), in the presence of 10% Pd on charcoal (40 mg) was hydrogenated in a Parr Apparatus at 40 psi and 30°C for 12 h The reaction mixture was

filtered from the catalyst and concentrated in vacuum giving **5c,6c**, mp 157 -158°C (from EtOH), IR ($CHCl_3$) 1704, 1640, 1602 cm^{-1}, for ^1H and ^{13}C NMR data - see Table 2, CIMS *m/z* 354 $[MH]^+$ (100%), Anal Found C, 54 63, H, 6 40, N, 12 10 $C_{16}H_{23}N_3O_6$ requires C, 54 38, H, 6 56, N, 11 89%.

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REFERENCES

1 Kagan, H. B , In *Comprehensive Organometallic Chemistry*, Wilkinson, G , Stone, F G A., Abel, E W Eds , *Asymmetric Catalysis*; Bosnich, B , Ed., Martinus Nijhoff Publishers Dordrecht, The Netherlands, 1986
Halpern, J , In *Asymmetric Synthesis*, Morrison, J D Ed., Academic Press New York, 1985, Vol 5
Koenig, K. E *Ibid.*
Brunner, H , In *Catalysis of Organic Reactions*; Blackburn, D W , Ed., Marcel Dekker New York, 1990, Chapter 1
James, B R., Joshi, A , Knintovics, P , Morris, R. H , Thorburn, I S *Ibid* Chapter 2,
Andrade, J G , Prescher, G , Nagel U *Ibid* Chapter 3

2 Osborn, J A., Ng Cheong Chan, Y *J Am Chem Soc* **1990**, *112*, 9400
Becalski, A. G , Cullen, W R., Fruzuk, M D, James, B R., Kang, G-J *Inorg Chem* **1991**, *30*, 5002

3 Patchornik, A., Berger, A., Katchalski, E *J Am Chem. Soc* , **1957**, *79*, 6416
Babad, E , Ben-Ishai, D *J Heterocycl Chem* **1969**, *6*, 236
Pratt, R. F , Kraus, K., K. *Tetrahedron Lett* **1981**, *22*, 2431

4 Altman, J , Shoef, N , Wilchek, M., Warshawsky, A *J Chem. Soc , Perkin Trans I* **1984**, 59
Altman, J , Wilchek, M. *Liebigs Ann Chem* **1989**, 493

5 Altman, J , Schuhmann, E , Karaghiosoff, K , Eichin-Karaghiosoff, E , Beck, W *Z Naturforsch* **1991**, *46b*, 1473
Lippart, S *J Pure Appl Chem* **1987**, *59*, 731

6 Yeh, S M , Sherman, D G , Meares, C F *Anal Biochem* **1979**, *100*, 152
Fritzberg, A. R., Abrams, P G , Beaumier, P L , Kassina, S , Morgan, C , Rao, T N , Reno, J M , Sanders, J A., Srinivasan, A , Wilburg, D S *Proc Natl Acad Sci , U S A* **1988**, *85*, 4025

7 Cox, J P L , Craig, A. S , Helps, I M , Jankowski, K. J , Parker, D , Eaton, M. A W , Millickan, A T , Millar, K., Beeley, N R. A , Boyce, B A *J Chem Soc Perkin Trans 1* **1990**, 2567

8 Carpino, L A. *J Chem Soc Chem Commun* **1966**, 858

9 Osborn, J A. Jardine, F H , Young, J F Wilkinson, G. *J Chem. Soc.* **1966**, 1711

10 Berkovich, E , Jacobson, A , Blum, J , Schumann, H , Schaeffers, M , Hemling, H. *J Organomet Chem.* **1992**, *436*, 95

11 Schrock, R. R., Osborn, J A. *J Am Chem Soc* **1971**, *93*, 2397

12 Glaser, R., Geresh, S , Blumenfeld, J *J Organometal Chem* **1976**, *112*, 355

13 Dang, T P , Kagan, H. B *J Chem Soc Chem Commun* **1971**, 481
Kagan, H B , Dang, T P *J Am Chem Soc* **1972** , *94, 6429*

14 Achiva, K *J Am Chem Soc* , **1976**, *98*, 8265

15 Valasinas, A , Frydman, B , Friedmann, H. C *J Org Chem* **1992** , *57*, 2158

16 Altman, J , Ben-Ishai, D *Tetrahedron Asymmetry* **1993**, *4 (in press)*

17 Pirkle, W , Hauske, J R. *J Org Chem* **1976**, *41* , 801, **1977**,*42*, 1839

18 Pauly, H *Hoppe-Seyler's Z Physiol Chem* **1904**, *42*, 508