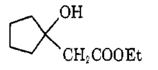
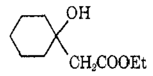
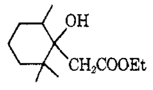
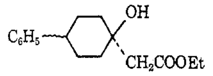
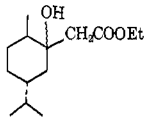
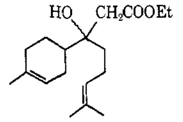
Table I
Reformatsky Reaction of Carbonyl Compounds with Zinc and Ethyl Bromoacetate

			Yield, %		
Carbonyl compd	Product	Bp, °C (mm)[a]	Zinc column[b]	Conventional method	TMB–THF method[c]
1-Butanal (**4**)	$CH_3(CH_2)_2CH(OH)CH_2COOEt$	45 (0.02)	89	69[d]	97
Cyclopentanone (**5**)		57 (0.03)	95	50[c]	93
Cyclohexanone (**6**)		66 (0.03)	93	56[e]	85
Benzaldehyde (**7**)	$C_6H_5CH(OH)CH_2COOEt$	95 (0.02)	94	61[e]	95
2,2,6-Trimethylcyclohexanone (**8**)		73 (0.02)	49	20[f]	
4-Phenylcyclohexanone (**9**)		70 (0.02)	96		
(−)-Carvomenthone (**10**)		126 (0.02)	83		
1-Methyl-4-(5-methylhex-4-enoyl)cyclohexene (**11**)		118 (0.02)	86		

[a] Analyzed sample. [b] Based upon glpc analysis using internal standards. [c] Data from ref 5. [d] Data from ref 4. [e] Data from ref 2. [f] This work.

zene and heated until refluxing benzene was just visible above the head of the column bed. A solution of 12.2 g (0.146 mol) of cyclopentanone and 48.6 (0.291 mol) of ethyl bromoacetate in 200 ml of dry benzene was added dropwise from the funnel at *ca.* 1 ml/min. The heat applied to the column was decreased by 25% soon after addition commenced to maintain a gentle reflux at the column head. After addition was complete, the column was flushed with 50 ml of benzene. The pale yellow solution which had collected was poured into 300 ml of ice-cold 15% sulfuric acid, and the mixture was shaken until the colorless precipitate had dissolved. The organic layer was separated and washed successively with saturated sodium bicarbonate solution and saturated sodium chloride solution. The benzene extract was dried ($MgSO_4$), the solvent was removed *in vacuo*, and the residue was distilled to give 23.6 g (95%) of **5**, bp 53–57° (0.03 mm).

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Registry No. 4, 2305-25-1; **5,** 3197-76-0; **6,** 5326-50-1; **7,** 5764-85-2; **8,** 42908-40-7; 1-butanal, 123-72-8; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; benzaldehyde, 100-52-7; 2,2,6-trimethylcyclohexanone, 2408-37-9; zinc, 7440-66-6; ethyl bromoacetate, 105-36-2.

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Synthesis of Menthyl- and Neomenthyldiphenylphosphine. Epimeric, Chiral, Tertiary Phosphine Ligands for Asymmetric Synthesis

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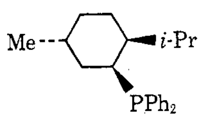
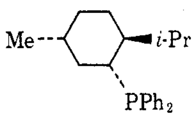
During the past several years the hydrogenation of unsaturated organic substrates using soluble transition-metal complexes as catalysts has been extensively studied. Numerous publications testify to the intrinsic interest and utility of homogeneous reducing systems.[1] Such systems are ideally suited for the introduction of chiral ligands which convey upon the transition metal complex the potential for diastereomeric interactions with unsaturated organic substrates, thus making asymmetric synthesis possible.[2] The realization of asymmetric synthesis in homogeneous hydrogenations,[3] hydrosilylations,[4] and hydroformylations[5] has been the subject of several recent papers.

In this paper we report details of the synthetic procedures for neomenthyldiphenylphosphine (NMDPP) and menthyldiphenylphosphine (MDPP), chiral tertiary phos-



NMDPP



MDPP

phine ligands that can be prepared in quantity from (−)-menthol *via* (−)-menthyl and (+)-neomenthyl chloride, respectively. Our initial syntheses of these ligands involved the reaction of lithium diphenylphosphide with neomenthyl or menthyl chloride in tetrahydrofuran solvent. Subsequently we have obtained much better results with sodium diphenylphosphide.[6]

Experimental Section

Diphenylphosphine.[7] Chlorodiphenylphosphine (908 g, 4.12 mol) was added to a stirred, ice-cold suspension of lithium aluminum hydride (47.1 g, 1.24 mol) in dry ether (2 l.) over a period of 1.5 hr, under nitrogen. The reaction mixture was allowed to stand overnight under nitrogen. It was then heated at reflux for 1 hr before water (110 ml) was added dropwise and reflux continued for an additional 3 hr. The ether layer was filtered through Celite (caution: after filtration the Celite cake may be pyrophoric) and the precipitate was washed well with ether. The combined ether solutions were concentrated under reduced pressure and distilled to give 565 g (74%) of diphenylphosphine, bp 99–100° (1 mm). Another 30 g of diphenylphosphine containing a trace of diphenylphosphine oxide was collected at a slightly higher temperature.

(+)-Neomenthyl chloride was prepared from (−)-menthol using the procedure of Horner, *et al.*[8]

(−)-Methyl chloride was prepared from (−)-menthol using the procedure of Smith and Wright.[9]

(+)-Neomenthyldiphenylphosphine. Sodium metal (34.5 g, 1.5 mol) was added in small pieces to 1.5 l. of anhydrous ammonia under a nitrogen atmosphere. Over a 1-hr period Ph_2PH (279 g, 1.5 mol), diluted to 600 ml with dry THF, was added to the sodium in ammonia solution (hydrogen evolution). The resulting red solution of sodium diphenylphosphide was allowed to warm to room temperature to expel the ammonia. A solution of (−)-menthyl chloride [262 g, 1.5 mol, $[\alpha]^{22}_{D}$ −49.1° (*c* 2.15, heptane), diluted to 800 ml with dry THF] was added in one portion. The reaction mixture was heated at reflux for 54 hr. The resulting light orange solution was treated with 250 ml of water. The organic layer was separated, washed with water, concentrated, and vacuum distilled until crystal formation was observed in the distillation condenser [about 160° (1 mm)]. The forerun was saved for recovery of diphenylphosphine.[10] The pot residue (260 g) was carefully recrystallized from 95% ethanol (degassed with N_2[11]) using 16 ml of solvent/g of crude phosphine and very slow cooling. The first crop of crystals (130.5 g) contained 85% NMDPP (glpc, 3% SE-30 on Varaport 30, 80–100 mesh, 235° 50 ml/min He flow rate) and 15% NMDPP oxide. The mother liquors were cooled further and yielded 46 g of crystals (94–95% NMDPP), $[\alpha]^{23}_{D}$ +94.4 (*c* 1.26, CH_2Cl_2), mp 96–99°.[12]

The mother liquor from the second crop of crystals was concentrated and cooled to give an additional 11 g of crystals [75% NMDPP, 10% NMDPP oxide, 15% $Ph_2P(O)H$]. The total conversion of menthyl chloride to NMDPP was about 34%, not counting the amount of NMDPP oxide produced. Careful recrystallization can provide high-purity NMDPP (95%), but the oxide is a tenacious impurity. Oxide does not interfere in the conversion of NMDPP to Rh(I) complexes of the Wilkinson type by displacement on μ-alkene Rh(I) precursors.[3g]

(+)-Neomenthyldiphenylphosphine Oxide. The mother liquor from the last crystallization of NMDPP described above was evaporated to dryness, and the residue was dissolved in chloroform and oxidized with bromine water to give crude NMDPP oxide, 21 g from xylene, mp 215–217°.

In another preparation, 5.0 g of impure NMDPP was treated with 10 ml of 30% H_2O_2 in a suspension containing 50 ml of benzene and 40 ml of 10% NaOH solution. After 18 hr the benzene layer was separated, washed with water, dried, and concentrated to give 3.3 g of crude NMDPP oxide. The crude material was crystallized from 30 ml of xylene to give crystals of NMDPP oxide, mp 216–217°, $[\alpha]^{29}_{D}$ +54.5° (*c* 1.40, absolute ethanol).

(−)-Menthyldiphenylphosphine. Sodium metal (23.0 g, 1.0 mol) was added in small pieces to 1 l. of anhydrous ammonia under a nitrogen atmosphere. When the sodium was dissolved, a solution of Ph_2PH (186 g, 1.0 mol), diluted to 400 ml with anhydrous THF, was added dropwise. An additional 400 ml of THF was added after addition of the Ph_2PH solution was complete. The red solution was then allowed to warm to room temperature. The resulting solution was warmed slightly to expel all the ammonia, and was then cooled in an ice bath. A solution of (+)-neomenthyl chloride [159 g, 0.91 mol, $[\alpha]^{22}_{D}$ +47.3° (*c* 3.08, heptane), diluted to 400 ml with anhydrous THF] was added over a 1-hr period. The reaction mixture was allowed to warm to room temperature slowly, stirred at room temperature for 3 hr, and then heated at reflux for 2 hr.

At the end of the reflux period, 200 ml of water was added to the light yellow reaction mixture. The organic layer was separated, washed with water, dried (Na_2SO_4), concentrated, and vacuum distilled (1 mm) until crystal formation was observed in the distillation condenser. The forerun was saved for recovery of diphenylphosphine. The pot residue weighed 95.0 g and was shown by glpc to be mainly menthyldiphenylphosphine. The total conversion of neomenthyl chloride to MDPP was about 25–30%.[13] The crude phosphine was recrystallized from 475 ml of degassed ethanol to give white crystals (27.8 g) which were isolated by vacuum filtration and dried under vacuum over P_2O_5. These crystals were shown by glpc to be 98% menthyldiphenylphosphine, $[\alpha]^{22}_{D}$ −93.9° (*c* 1.67, CH_2Cl_2),[14] mp 57.5–58.5°. On further cooling the mother liquor yielded an additional 25.5 g of crystals, 96% MDPP by glpc.

(−)-Menthyldiphenylphosphine Oxide. The ethanol filtrate from the above crystallizations was concentrated and the residue was dissolved in 200 ml of $CHCl_3$ and treated with bromine water until an orange color persisted. The organic phase was separated, washed twice with 100 ml of 5% NaOH and twice with 100 ml of water, dried ($NaSO_4$), and concentrated to give crude MDPP oxide (27.5 g). Crystallization from toluene gave MDPP oxide, mp 183.5–185°, $[\alpha]^{25}_{D}$ −87.4° (*c* 1.74, absolute ethanol).

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Registry No. (+)-NMDPP, 43077-29-8; (+)-NMDPP oxide, 43077-30-1; (−)-MDPP, 43077-31-2; (−)-MDPP oxide, 43077-32-3; sodium diphenylphosphide, 4376-01-6; (−)-menthyl chloride, 16052-42-9; diphenylphosphine, 829-85-6; (+)-neomenthyl chloride, 13371-12-5.

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(10) The foreruns from the work-up of NMDPP and MDPP syntheses were redistilled to recover diphenylphosphine. The fraction boiling at 99–100° (1.0 mm) was collected.

(11) Precautions should be taken during all stages of the work-up of NMDPP and MDPP to limit contact with air as much as possible, and thus reduce the amount of oxide formed as a by-product.

(12) Melting points of NMDPP and MDPP samples vary slightly from preparation to preparation depending on the amount of oxide present.

(13) Methenes and diphenylphosphine are by-products in the sodium diphenylphosphide reactions. These products apparently result from elimination reactions in which the phosphide anion functions as a base rather than as a nucleophile. The elimination side reactions are the primary reason for the relatively low yields of the desired tertiary phosphines. Elimination is, as expected, a more serious competitive process in the case of neomenthyl chloride. The diphenylphosphine, which results from the elimination reaction and hydrolysis of unreacted sodium diphenylphosphide, can be recovered.[10]

(14) There is a recent literature report,[4b] without experimental details, that gives $[\alpha]^{20}\text{D}$ −95.7° (c, 1.07, CH_2Cl_2).

The 1,3,5-Trinitrobenzene–*N*-Methylanilide σ Complex

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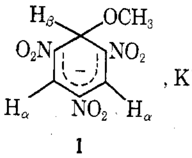
While σ complex formation between polynitroaromatic compounds and aliphatic amines has been well established,[1,2] only one instance of a σ complex involving an aromatic amine has been reported.[3] In the previous communication[3] we presented spectral evidence (nmr and uv-visible) which strongly suggested that the product of the reaction between the methoxide ion–1,3,5-trinitrobenzene (TNB) σ complex **1** and aniline in dimethyl sulfoxide (DMSO) solution was the anilide σ complex **2**.

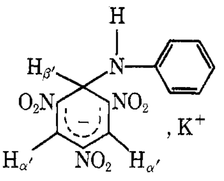
In an effort to confirm our earlier conclusions, we have extended the study to include the reaction of **1** with *N*-methylaniline. It was envisaged that use of this amine would result in an unambiguously interpretable nmr spectrum, since the NH-$H_{\beta'}$ coupling which was evident in **2** will have been removed in the anticipated σ complex **3**. Our previous findings of a relatively sharp AB quartet with a large coupling constant for the σ complex **2** was unexpected, as the observation of sharp doublets for NH protons coupled to CH is a relatively rare occurrence.[4,5] In view of the fact that we are concerned with structural identification of a novel complex, it was desirable to have at least one case where this feature would be absent from the nmr spectrum. In practice it turned out that the choice of *N*-methylaniline was only partially successful, as a result of interference from the aromatic protons of the amine; however, use of *N*-methylaniline-*2,4,6-d*$_3$ led to the desired simplification in the nmr spectrum and has thus allowed complete structural identification of the aryl amine σ complex.

After **1** was mixed with *N*-methylaniline in DMSO solution the following nmr spectral changes were observed. A spectrum taken 45 min after mixing exhibited the H_α, H_β, and OCH_3 absorptions typical for **1** at 8.48 (doublet, J = 1.2 Hz), 6.16 (unresolved triplet), and 3.20 ppm (singlet), respectively; and for *N*-methylaniline typical multiplets in the aromatic proton region due to the ring protons, a broad singlet at 5.4 ppm for the amino proton, and a doublet (J = 5 Hz) centered at 2.63 ppm attributed to the *N*-methyl group. In addition there were present a small signal 0.05 ppm downfield from H_α and assigned to $H_{\alpha'}$ of **3**, and a singlet at 2.30 ppm which corresponds to the methyl protons in the *N*-methylaniline moiety of **3**. With time further development was evident for the peaks attributed to **3** and those due to methanol (quartet, J = 5 Hz at 4.0 ppm; doublet, J = 5 Hz at 3.1 ppm), while those belonging to **1** and *N*-methylaniline steadily decreased. The changes were observed to be complete within 1 day.

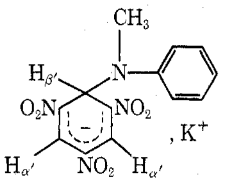
The signal expected for $H_{\beta'}$ in **3** was not observed, implying that it is "buried," likely under the aromatic proton multiplets which are centered at *ca.* 6.8 ppm. In order to locate the position of the $H_{\beta'}$ absorption, *N*-methylaniline-*2,4,6-d*$_3$ was treated with **1**. In DMSO solutions the 3 and 5 protons in the *N*-methylaniline-*2,4,6-d*$_3$ give rise to a single peak at 7.03 ppm. On reaction of this amine with **1**, two new features are discernible from the nmr spectra. Firstly, a peak at 7.13 ppm increases at the expense of the signal at 7.03 ppm and is assignable to the ring protons in the partially deuterated *N*-methylaniline moiety of the complex **3**. Secondly, the growth in a peak at 6.63 ppm corresponds to the decrease in intensity of the H_β signal and is assigned to $H_{\beta'}$. Thus the nmr parameters for the σ complex can be assigned: $H_{\alpha'}$ 8.53 ppm, $H_{\beta'}$ 6.63 ppm, NCH_3 2.30 ppm.



1



2



3

The reaction between *N*-methylaniline and **1** in DMSO was also followed by means of visible spectroscopy. Using solutions of comparable concentrations to those used in the nmr experiments, visible spectra were recorded periodically, following a 100-fold dilution with DMSO. The reaction was observed to be accompanied by a decrease in the 427- and 509-nm absorptions due to **1** and the development of absorption maxima at 436 and 516 nm due to product formation. Interconversion of the two absorbing species was characterized by reasonably tight isosbestic points. The double absorptions with the higher energy maximum being more intense are of course typical of σ complexes of TNB.[6-9]

The nmr and visible absorption spectral data presented above are fully consistent with the formation of the σ complex **3**. It may be concluded that the reaction of the TNB–methoxide ion complex **1** with primary or secondary aromatic amines in DMSO solution, leading to formation of TNB–aryl amine σ complexes, appears to be a general type of reaction.

Further examination of the nmr parameters for the complex **3** reveals additional information with probable structural significance. It will be noted that the nmr peaks of protons in the aromatic amine are shifted to low field on complex formation. This may be ascribed to the electron-withdrawing ability of the 2,4,6-trinitrocyclohexadienate moiety relative to an amino proton. Contrasting to the low-field shift of the aromatic protons of the amine moiety is the observed shift to high field of the *N*-methyl proton resonance on formation of **3**. This observation suggests that the methyl group protons experience an an-