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STEREOCHEMISTRY OF REDOX-DEMERCURATION OF AN OPTICALLY ACTIVE 8-(α-BROMOMERCURIETHYL)QUINOLINE WITH ZEROVALENT PALLADIUM COMPLEXES *

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Summary

A novel organomercurial bearing the metal atom at a chiral centre, 8-(α-bromomercuriethyl)quinoline (I) has been synthesized from the respective bromide and metallic mercury, and resolved via diastereomeric D-camphor sulphonates. Enantiomeric I has been treated with $(Ph_3P)_4Pd^0$ and $(dba)_3Pd_2^0$ to give optically active chelate metallocycles II and III which had been previously known in racemic form. In both reactions, (—)I leads to (+)organopalladiums. The optical activity proves the heterolytic reaction mechanism.

Introduction

Some years ago we discovered the reaction of organic and organometallic mercury(II) derivatives with zerovalent complexes of platinum and palladium [1]. This reaction has subsequently been investigated in some detail [2]. The first step is insertion of the L_2M^0 moiety into the mercury—element bond, with concurrent change of the valence state of the platinum metal. The second step when it does occur is elimination of the mercury. The overall process may be called redox demercuration using low-valent metal complexes.

$$R—Hg—R' + L_nM^0 \rightarrow R—Hg—ML_2—R' \rightarrow R—ML_2—R'$$

This reaction was shown to exhibit important differences from the well-known oxidative addition of organic halides to zerovalent complexes, including the formation of bimetallic intermediates and bis-organyl derivatives as final products. In this connection, the stereochemistry of this reaction is of great

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interest since the stereochemistry of oxidative addition of organic halides is still a subject of discussion.

In a recent work [3] we have presented some indirect evidence that in the case of diastereomeric L-menthyl esters of α-bromomercuriphenylacetic acid the overall process results in the net retention of configuration of the carbon chiral centre. It seems, however, that enantiomeric models would be more conclusive and therefore preferable. The detailed discussion concerning the choice of model compounds has been done elsewhere [3]. In this paper, we wish to report the synthesis of both enantiomers of an organomercurial which is the precursor of the stable chiral chelated metallocycles and thus can serve as a useful model for stereochemical study.

Synthesis and resolution of the model organomercurial

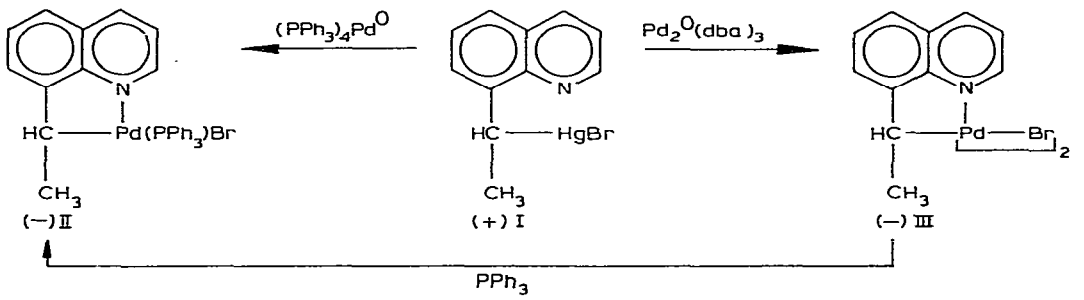
Some time ago we reported cyclometallation of the alkyl group of 8-alkylquinoline as a way to form chiral organopalladiums. One of these has been prepared in optically active form [4]. Later, the oxidative addition of benzylic-type bromides was shown to be a more useful experimental procedure [5].

That time, however, no organomercurials were prepared in this series. Very recently, we have found that the classical method, namely, the reaction of benzylic bromides with metallic mercury [6] is successful in the synthesis of the desired organomercurial derivatives of 8-alkylquinolines [7]. As nitrogen heterocycles they are bases and form salts with acids. Thus chiral organomercurial I has been resolved partially as the D-camphor sulphonate [8], as it was done before with 8-(α-bromoethyl)quinoline [8]. The mixture of diastereomeric salts from I enriched in the (+)-enantiomer has been isolated, $[\alpha]^{20}_{578}$ +10.9° $[\alpha]^{20}_{589}$ +10.2° (CH_2Cl_2, *c* 1.3). It exhibited in its ^1H NMR spectrum (250 MHz) two methyl doublets as assigned using double resonance. Based on their intensity the ratio of diastereomers has been estimated. Enantiomeric excess in that sample of I was 57.2% based on the absolute rotation of the pure enantiomer $[\alpha]^{20}_{578}$ 19.1°; $[\alpha]^{20}_{589}$ 17.5° (CH_2Cl_2). Subsequent crystallization of an enriched sample from a mixture of dichloromethane/hexane afforded I, $[\alpha]^{20}_{578}$ +19.4° (CH_2Cl_2, *c* 1.14), which seems to be optically pure.

Reaction of enantiomeric 8-(α-bromomercuriethyl)quinoline with tetrakis-(triphenylphosphine)palladium and tris(dibenzylideneacetone)dipalladium

Optically active (+)I reacts rapidly with $(Ph_3P)_4Pd$ in benzene with complete elimination of mercury to give known [4] chelated σ-organopalladium which possesses optical activity, (—)II. Similarly, (+)I with $Pd_2(dba)_3 \cdot CHCl_3$ afforded (—)III. A sample of (+)III, $[\alpha]^{20}_{578}$ +3.2° (*c* 0.87) has been converted into (+)II, $[\alpha]^{20}_{578}$ +5.1° (*c* 1.64) by direct treatment with Ph_3P. This reaction confirmed the same configuration of the carbon atom in both (+)II and (+)III.

The L_2Pd insertion is known to proceed into both Hg—Hal and Hg—C bonds, the former being predominant [3]. The first pathway gives the intermediate CHgPdHal. In the course of the mercury atom extrusion the stereochemical configuration of carbon should be lost. There is no precedent in the literature that demercuration would occur without complete racemization of the chiral



carbon centre involved. However, demercuration of the isomeric intermediate CPdHgHal which results from the second (minor) pathway, on the contrary, will not change the carbon configuration which is determined exclusively by the steric course of the insertion step. In fact, any optical activity observed in organopalladiums II and III must result from this second pathway. In the earlier paper [4], the higher rotational angle, $[\alpha]_{589}^{20}$ +41.5° (CH_2Cl_2) for the respective chloride (II, Cl instead of Br) was achieved through resolution via the diastereomeric complexes with α-phenylethylamine.

The absolute configurations of I and II are now under study in order to establish the exact stereochemical sense of the stereoselective pathway of redox demercuration.

Experimental

All reactions with palladium(0) complexes were performed under argon in dry solvents. Melting points measured in sealed capillaries are corrected. ^{1}H NMR spectra were recorded on a Hitachi Perkin—Elmer R12 (60 MHz) and Bruker WM250 (250 MHz) spectrometers. ^{31}P NMR spectra were obtained on a Bruker HX90 with 85% H_3PO_4 as external standard. Optical rotations were taken at 20°C with a Perkin—Elmer 241 polarimeter in CH_2Cl_2 as solvent. Palladium(0) complexes were prepared using the known procedures [9,10].

Racemic 8-(α-bromomercuriethyl)quinoline, (±) I. A mixture of 8-ethylquinoline (13.25 g, 6% of quinoline) and *N*-bromosuccinimide (15.75 g) in 50 ml of CCl_4 was refluxed for 1.5 h in the presence of catalytic quantities of $(PhCO_2)_2$ [5]. Succinimide was filtered from the cooled solution which was then evaporated in vacuo. Metallic mercury was added to the crude 8-(α-bromoethyl)quinoline thus prepared. The resulting mixture was shaken for 3 h and then extracted with dichloromethane (1.5 l). The crude organomercurial was obtained after removal of solvent and washing with pentane. Crystallization from CH_2Cl_2 removed coloured by-products to give white crystals of (±)I. The yield was 23.75 g (68%), m.p. 152°C, lit. [7] 157°C.

Resolution of racemic I into enantiomers by using (+)-D-camphor-10-sulphonic acid. To a solution of (±)I (3.4 g) in ethyl acetate (300 ml) was added 2.0 of (+)D-camphor-10-sulphonic acid, $[\alpha]_{589}^{20}$ +20° (H_2O) in acetonitrile (20 ml). After 2 h a slight precipitate was removed and 120 ml of pentane was added. The resulting solution was chilled to —12°C. A small quantity of dark oil which separated was discarded. The clear yellow-green solution was diluted with 20 ml of hexane and left for 24 h at —78°C. A yellow oily salt was separated and

treated with ethanol (50 ml) and aqueous $NaHCO_3$ to liberate the organomercurial base from the salt. This afforded white solid (+)I (1.32 g, 39%), $[\alpha]_{578}^{20}$ 8.0° (*c* 1). This sample was dissolved in CH_2Cl_2 (70 ml) and hexane (50 ml) was added to the filtered solution. After 1 h, at —78°C crystals of racemic (±)I were obtained which are less soluble. Evaporation of mother liquor yielded 0.30 g of more soluble, presumably optically pure (+)I, $[\alpha]_{578}^{20}$ +19.4° (*c* 1.14).

Evaporation of the initial filtrate after the separation of oily salt gave diastereomeric salt of (—)I which was treated as described above to afford 1.56 g of (—)I, $[\alpha]_{578}^{20}$ —5.7° (*c* 2.12). In order to increase the optical purity, this sample was dissolved in 90 ml of CH_2Cl_2 and 40 ml of hexane. After the separation of some racemic I, the (—)enantiomer was isolated at —78°C, $[\alpha]_{578}^{20}$ —9.0°, (*c* 1.71), m.p. 132°C (dec.).

Analyses for the diastereomeric camphor sulphonate triturated with pentane and dried in vacuo were C, 39.08; H, 4.28; Hg, 27.27. $C_{21}H_{26}BrHgNO_4S \cdot 1/2\ CH_3COOC_2H_5$ calcd.: C, 38.75; H, 4.23; Hg, 28.05%.

Reaction of racemic and optically active 8-(α-bromomercuriethyl)quinoline with $Pd(PPh_3)_4$. $Pd(PPh_3)_4$ (1.15 g) and 0.42 g of (—)I, $[\alpha]_{578}^{20}$ —9.0° (*c* 1.7) were dissolved by stirring in 30 ml of benzene. The mercury separation was completed during 10 min. After 1 h the solution was filtered. The product, triphenylphosphine-(8-ethylquinoline-α-*C*,*N*)palladium bromide, (+)II, was obtained on cooling by slow addition of hexane. The yield was 0.46 g (79%), $[\alpha]_{578}^{20}$ +6.9° (*c* 1), m.p. 125—130°C (dec.) Analyses: found: C, 61.12; H, 4.68; Br, 12.45. $C_{25}H_{25}BrNPPd$ calcd.: C, 61.55; H, 4.34; Br, 11.70%. NMR (CH_2Cl_2): ^1H, δ 1.02 ppm, ^{31}P, δ 34.8 ppm; $^3J(HH) = {}^4J(HP) = 6.6$ Hz.

Reaction of racemic and optically active 8-(α-bromomercuriethyl)quinoline with $Pd_2(dba)_3 \cdot CHCl_3$. The palladium complex (1.3 g) and 1.0 g of (±)I were stirred as a suspension in 50 ml of benzene. The red-violet solution gradually turned yellow. After 90 min a black precipitate was separated (0.5 g). From the chilled filtrate yellow crystals of (±)III were obtained (0.56 g). The mother liquor was evaporated to dryness and dibenzylideneacetone was washed out with ether to give additional product. The total yield was 0.61 g (81%), m.p. 147°C (blackened), 164°C (dec.). Anal.: found: C, 38.69; H, 3.20. $C_{22}H_{20}Br_2N_2Pd_2$ calcd.: C, 38.57; H, 2.94%.

Similarly, 0.218 g of (+)I, $[\alpha]_{578}^{20}$ +19.4° (*c* 1.14) and 0.259 g of $Pd_2(dba)_3 \cdot CHCl_3$ in 30 ml of benzene afforded (—)III, $[\alpha]_{578}^{20}$ —8.5° (*c* 0.76) which blackened at 147°C, dec. 164°C.

Reaction of optically active III with triphenylphosphine. Triphenylphosphine (0.065 g) and 0.080 g of (+)III, $[\alpha]_{578}^{20}$ +3.23°, prepared from (—)I, $[\alpha]_{578}^{20}$ —9.1°, were dissolved in CH_2Cl_2 (10 ml). After 30 min the light yellow solution was evaporated to dryness. The residue was treated with hexane (3 × 8 ml) to give (+)II, chromatographically identical to that described above, R_f 0.13 (Silufol UV-254, eluent CH_2Cl_2), $[\alpha]_{578}^{20}$ +5.1° (*c* 1.64).

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