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Stereochemistry of the Exchange Reaction between Lithium Tetrachloropalladate and Alkylmercury Compounds

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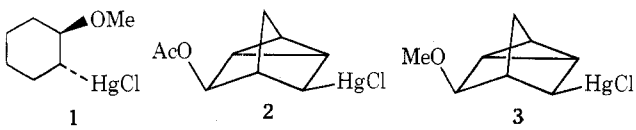
The carbomethoxylation of several σ-bonded organomercurials (derived from the oxymercuration of cyclohexene and norbornadiene) in the presence of stoichiometric amounts of lithium tetrachloropalladate and carbon monoxide was found to proceed with predominant retention of configuration at carbon. Since the carbomethoxylation of alkylpalladium compounds occurs with complete retention of configuration at carbon, therefore the exchange of palladium for mercury occurs with predominant retention of configuration.

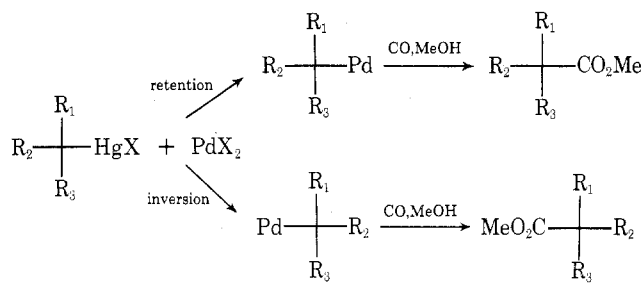
The organometallic exchange reaction is a generally employed method for the generation of transition metal–carbon σ bonds[1] and the formation of σ-bonded organopalladium complexes *via* palladium exchange with organomercurials has been used extensively in the arylation, methylation, and carbomethoxylation of olefins.[2-5] Alkylmercury compounds of known configuration can be readily obtained *via* the solvomercuration of olefins and the stereochemistry of addition to simple olefins is trans.[6] The exchange of palladium for mercury is, therefore, a possible method of stereospecifically synthesizing palladium–carbon σ-bonded complexes. The stereochemistry of the exchange process can be determined by trapping the unstable alkylpalladium intermediate with carbon monoxide in methanol[5] since the conversion of alkylpalladium complexes to esters has been shown to proceed with complete retention of configuration at the carbon bearing the metal.[7] Structural analysis of the methyl ester formed would establish the stereochemistry of the exchange reaction. (See Scheme I.)

Thus, the carbonylation of alkylmercury compounds **1**,[8] **2**,[9] and **3**,[10] in the presence of lithium tetrachloropalladate



1 2 3

Scheme I

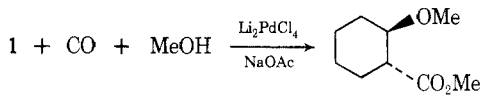


in methanol was investigated to determine the stereochemistry of the exchange process.

Results and Discussion

The carbonylation of *trans*-2-methoxycyclohexylmercuric chloride (1) in methanol in the presence of sodium acetate was effected by treatment of **1** with lithium tetrachloropalladate and carbon monoxide (1 atm) at room temperature. The reaction afforded methyl *trans*-2-methoxycyclohexylcarboxylate (**4**)[5] in a 7% yield. No attempts were made to isolate low-boiling organic products which were removed during the work-up. The low yield of **4** suggests the carbonylation did not compete favorably with the decom-

position of the unstable organopalladium intermediate *via* β-palladium hydride elimination.



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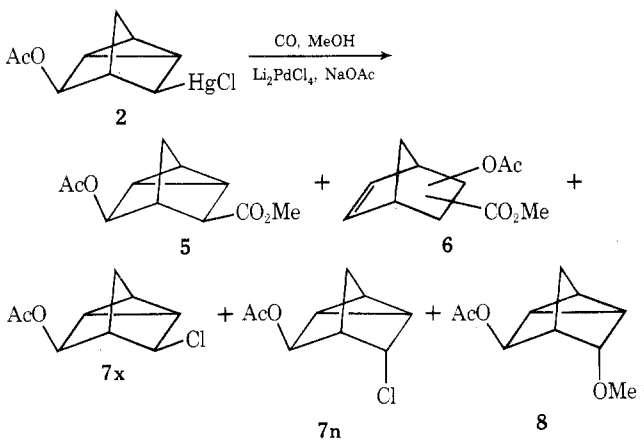
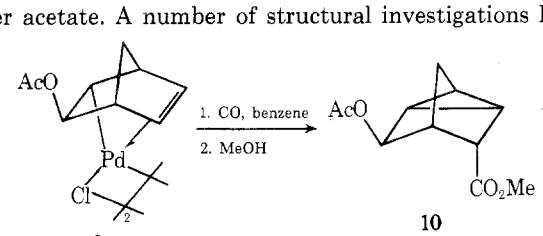
Carbonylation of *exo,exo*-3-acetoxynortricyclyl-5-mercuric chloride (**2**) gave a product mixture consisting of 64% *exo,exo*-3-acetoxy-5-carbomethoxynortricyclene (**5**), 8% acetoxycarbomethoxynorbornene (**6**), 14% *exo,exo*-3-acetoxy-5-chloronortricyclene (**7x**), 7% *exo,endo*-3-acetoxy-5-chloronortricyclene (**7n**), and 6% *exo,endo*-3-acetoxy-5-methoxynortricyclene (**8**) in a total yield of 61%.



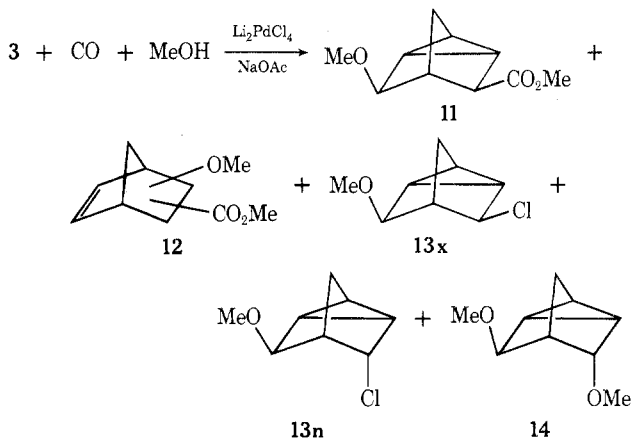
The exo,exo geometry at the 3 and 5 positions of **5** was assigned on the basis of chemical shift data. It has been well documented that in 3,5-disubstituted nortricyclenes, endo substitution at the 5 position produces a paramagnetic shift of the 3-endo proton, whereas exo substituents at the 5 position have negligible effect on the chemical shift of the 3-endo proton.[7,9,11] The chemical shift value of the C_3 methine proton (δ 4.65) of **5** was almost identical with that of the corresponding proton of **7x**[9] (δ 4.62), but upfield of the C_3 methine proton resonance (δ 4.93) of *exo,endo*-3-acetoxy-5-carbomethoxynortricyclene (**10**) owing to the "nearest-neighbor" deshielding effect. The endo methyl ester **10** was independently synthesized by the carbonylation of the σ-bonded palladium complex **9** obtained from treatment of dichloro(norbornadiene)palladium(II) with silver acetate. A number of structural investigations have



established that oxypalladation of palladium(II)–diolefin complexes proceeds trans with the oxo group exo and the metal endo or inside in each case.[12–15] The structure **10** was established on the basis that the analogous methoxyenyl complex underwent carbonylation to afford *exo,endo*-3-methoxy-5-carbomethoxynortricyclene.[7]

Nmr and mass spectral analyses showed that **6** had the gross structure shown; however, the positions of the acetoxy and carbomethoxy substituents could not be elucidated. The nortricyclyl chlorides **7x** and **7n** were identified by nmr and vpc comparison with authentic samples.[9] The nmr spectrum of **8** was in good agreement with the assigned exo,endo structure; the signal for the proton on the carbon bearing the acetoxy group (δ 5.13) was downfield from the corresponding proton resonances in **5** and **7x** (δ 4.65 and 4.62, respectively) due to the deshielding of the endo methoxy group.

The carbonylation of *exo,exo*-3-methoxynortricyclyl-5-mercuric chloride (**3**) afforded a 41% yield of a product mixture consisting of 34% *exo,exo*-3-methoxy-5-carbomethoxynortricyclene (**11**), 10% methoxycarbomethoxynorbornene (**12**), 31% *exo,exo*-3-methoxy-5-chloronortricyclene (**13x**), 18% *exo,endo*-3-methoxy-5-chloronortricyclene (**13n**), and 5% *exo,endo*-3,5-dimethoxynortricyclene (**14**).



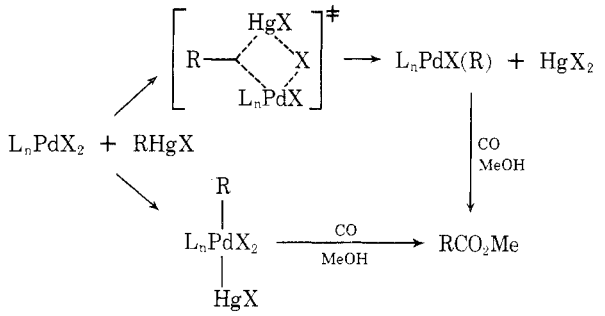
Identification of the ester **11** and the chlorides **13x**[16] and **13n**[11] was made by vpc and nmr comparison with authentic samples. The exo,endo stereochemistry of the diether **14** was inferred from nmr chemical shift data which showed that the absorption for the proton on the carbon bearing the exo methoxy group (δ 3.97) was shifted downfield relative to the corresponding proton signal (δ 3.32) of *exo,exo*-3,5-dimethoxynortricyclene.[16] The norbornene skeleton for **12** was established by nmr analysis, although the positions of the methoxy and carbomethoxy substituents could not be elucidated.

The absence of endo nortricyclyl methyl esters from **2** and **3** suggests that the palladium–mercury exchange process does not involve intermediate carbon-free radicals. The reduction of **2** by sodium borohydride has been shown to proceed *via* radical intermediates.[17] When the reduction was carried out with sodium borodeuteride, deuterium was shown to be incorporated about equally among the 5-exo and 5-endo positions of 3-acetoxynortricyclene.[17]

The predominant retention of configuration at carbon during the carbomethoxylation of **1**, **2**, and **3** is consistent with either a four-center[18] bimolecular electrophilic exchange of palladium for mercury or an oxidative addition of organomercury compounds to a palladium(II) species with retention of configuration at carbon. The oxidative addition of an organomercury compound to a d^8 transition metal complex to form a bimetallic complex containing a carbon–transition metal σ bond has been observed in fact, for a d^8 rhodium complex.[19]

The stereospecific formation of **4** could be the consequence of factors extraneous to the reaction mechanism. Although an interaction between palladium and methoxy could favor the formation of a *trans*-methoxycyclohexylpalladate intermediate (which upon carbonylation would form the trans ester **4**), an ether oxygen is a poor nucleophile. Extraneous electronic and steric effects are unlikely to be responsible for the formation of the exo esters **5** and **11**. The "endo protection" often observed in the norbornyl system does not exist here since the nortricyclene skeleton possesses C_{3v} symmetry. (See Scheme II.)

Scheme II



The rearranged esters **6** and **12** could arise from three possible pathways as illustrated for **2** in Scheme III. Path A involves an initial exchange of palladium for mercury with retention of configuration followed by the rearrangement of the intermediate alkylpalladium complex in a manner reminiscent of the interconversion of cyclopropylmethyl and 3-buten-1-yl Grignard reagents.[20] The rearrangement may be regarded formally as a cis β elimination of a palladium alkyl to give the norbornenylpalladium intermediate **15**. Subsequent carbomethoxylation with retention of configuration at carbon[7] would afford *endo,syn*-2-carbomethoxy-7-acetoxynorborn-5-ene (**6a**) as the rearranged ester. Alternatively, the exchange of palladium for mercury may proceed partially with inversion of configuration to afford a nortricyclylpalladium intermediate which rearranges to the norbornenylpalladium complex **16** (path B). Replacement of palladium with the carbomethoxy group with retention of configuration would give *exo,endo*-2-acetoxy-3-carbomethoxynorborn-5-ene (**6b**) as the rearranged ester. In path C, a palladium species inserts into a cyclopropane carbon–carbon single bond *via* oxidative addition to give an unstable palladium(IV) intermediate which decomposes to the norbornenylpalladium(II) complex **16**. Subsequent carbomethoxylation would afford **6b** as the rearranged ester. Insertion of d^8 complexes of platinum and rhodium into cyclopropane rings has been observed.[21]

Nmr double resonance results are compatible with the structure **6a**. In the nmr spectrum of **6**, a doublet of doublets (J = 12.5 Hz, 4.0 Hz) centered at δ 1.54 and a doublet of multiplets (J = 12.5 Hz) centered at δ ~2.0 may be assigned to the two methylene protons H_C and H_B of **6a**, respectively, on the basis of their relative chemical shifts[22] (Figure 1). Irradiation of H_D (δ 3.15) removed the 4-Hz splitting of the H_C signal. The value of 4.0 Hz for J_{CD} is in agreement with trans endo–exo coupling constants observed for systems of similar structure.[23,24] Since vicinal coupling constants between the bridgehead protons and the C_7 bridge protons in norbornene systems are in the range of 0–2 Hz[23,24] and no coupling exists between the C_2 exo proton and the C_7 bridge protons, the structure **6b** is therefore incompatible with the double-irradiation results.

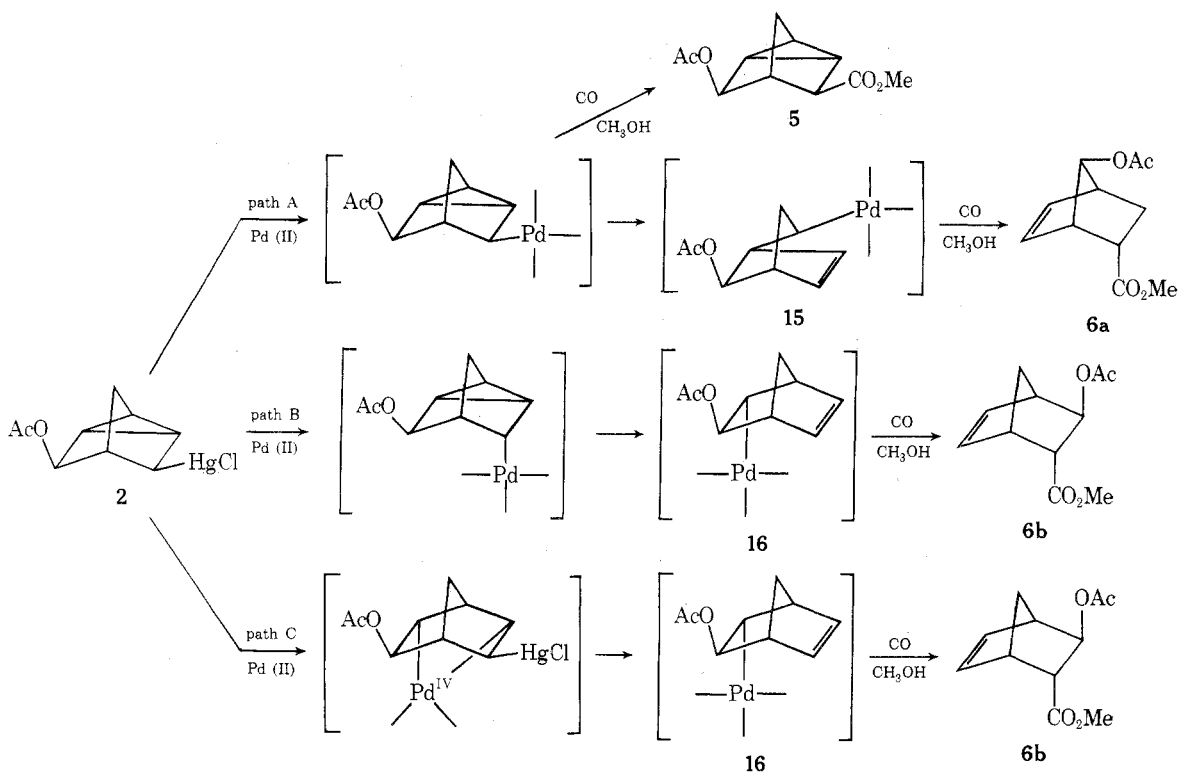
Increasing the carbon monoxide pressure (3 atm) in the carbonylation of **3** reduced the formation of the rearranged ester **12** to a trace amount. This observation is consistent with path A in which the nortricyclylpalladium intermediate can either undergo carbonylation to afford **11** or rearrange to a norbornenylpalladium complex to yield **12**. Increasing the carbon monoxide pressure increases the rate at which the nortricyclylpalladium complex is trapped, thus suppressing the formation of the rearranged ester **12**. Neither path B nor path C would exhibit such a carbon monoxide pressure effect on the rearrangement.

The nonester products were most likely obtained from the decomposition of and nucleophilic displacements on the intermediate alkylpalladium complexes.

Experimental Section

Preparation of Di-μ-chloro-bis(6-acetoxybicyclo-[2.2.1]hept-2-ene-*endo*-5σ,2π)dipalladium(II) (9). The preparation of this compound was carried out using a procedure similar to that described for the acetoxylation of dichloro(1,5-cyclooctadiene)palladium.[25] A mixture of 1.0 g (3.8 mmol) of dichloro(norbornadiene)palladium(II)[26] and 0.64 g (3.8 mmol) of silver acetate

Scheme III



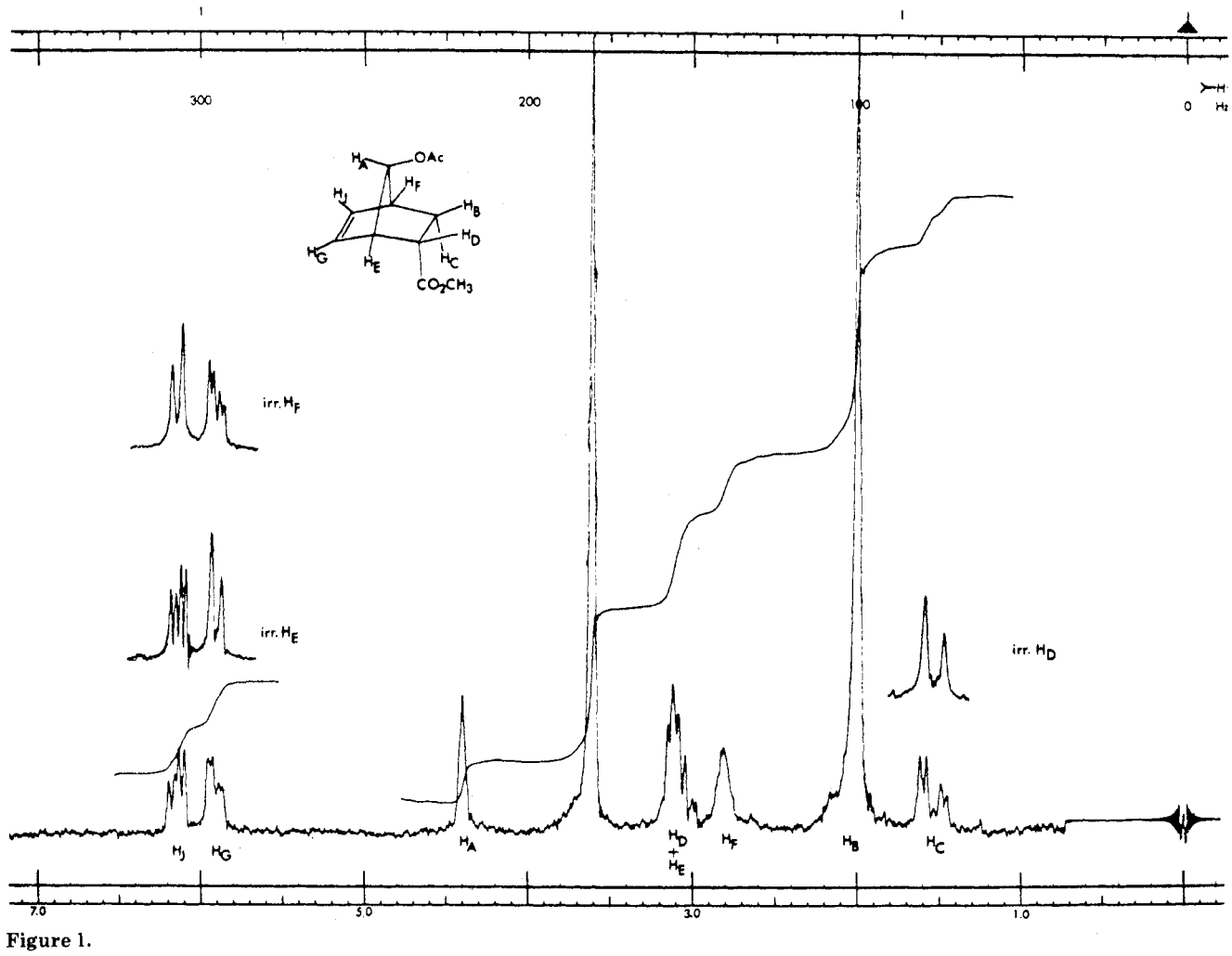


Figure 1.

in 200 ml of chloroform was stirred at room temperature for 1 hr. The silver salt was removed and the filtrate was concentrated under reduced pressure. The residue was triturated with ether and the resulting cream-colored complex was collected by gravity filtration to afford 0.7 g (1.2 mmol, 63%) of **9**. *Anal.* Calcd for $C_9H_{11}ClO_2Pd$: C, 36.86; H, 3.75. Found: C, 35.52; H, 3.63.

Carbonylation of Di-μ-chloro-bis(6-acetoxybicyclo-[2.2.1]hept-2-ene-*endo*-5σ,2π)dipalladium(II) (9). Formation of *exo,endo*-3-Acetoxy-5-carbomethoxynortricyclene (10). A mixture of 0.5 g (0.85 mmol) of **9** and 0.5 g (6.1 mmol) of sodium acetate in 120 ml of benzene was stirred under an atmosphere of carbon monoxide at room temperature for 3 hr. To the resulting mixture was added 50 ml of methanol. After 8 hr at room temperature, the reaction mixture was filtered gravimetrically to remove palladium metal. The filtrate was concentrated under reduced pressure and the residue was extracted with several small portions of ether. The combined ether extracts were washed with aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of ether under reduced pressure gave 0.23 g of an oil which was purified by preparative vpc using a 10 ft × ⅜ in. 20% DEGS/Chromosorb W column to afford **10:** nmr ($CDCl_3$) δ 4.93 (t, 1, AcOCH), 3.69 (s, 3, OCH_3), 2.51 (t, 1, CH_3O_2CCH), 2.31 (bs, 1), 2.02 (s, 3, CH_3CO_2), 1.90 (m, 1), and 1.3–1.7 ppm (4); mass spectrum (70 eV) *m/e* 210 (M^+).

Carbonylation of *trans*-2-Methoxycyclohexylmercuric Chloride (1). To a mixture of 3.57 g (10 mmol) of **1**[8] and 2.0 g (24.4 mmol) of sodium acetate in 30 ml of methanol was added a solution of 1.77 g (10 mmol) of palladium chloride and 0.85 g (20 mmol) of lithium chloride in 100 ml of methanol under an atmosphere of carbon monoxide. The reaction mixture was stirred at room temperature under carbon monoxide for 10 hr and then filtered gravimetrically to remove the precipitated metal and salts. The colorless filtrate was concentrated under reduced pressure and the residue was extracted with several small portions of pentane. The combined pentane extracts were washed with aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of pentane under reduced pressure afforded 0.13 g (0.7 mmol, 7%) of a liquid which was identified as methyl *trans*-2-methoxycyclohexylcarboxylate (**4**)[5] by vpc and nmr comparison with an authentic sample: nmr ($CDCl_3$) δ 3.68 (s, 3, CO_2CH_3), 3.42 (s, 3, OCH_3), 3.42 (m, 1, CH_3OCH), and 2.7–0.8 ppm (9).

Carbonylation of *exo,exo*-3-Acetoxynortricyclyl-5-mercuric Chloride (2). The carbonylation of a mixture of 4.37 g (11.28 mmol) of **2**,[9] 2.0 g (11.28 mmol) of palladium chloride, 1.0 g (23.6 mmol) of lithium chloride, 2.0 g (24.4 mmol) of sodium acetate, and 150 ml of methanol was effected in a manner described above to afford 1.4 g of organic products consisting of five components. The products were separated by vpc using a 20 ft × ⅜ in. 30% DEGS/Chromosorb W column. Two of the minor components were identified as *exo,exo*-3-acetoxy-5-chloronortricyclene (**7x**) (14%) and *exo,endo*-3-acetoxy-5-chloronortricyclene (**7n**) (7%), respectively, by nmr comparison with authentic samples.[9] A third nonester product was assigned the structure *exo,endo*-3-acetoxy-5-methoxynortricyclene (**8**) (6%): nmr ($CDCl_3$) δ 5.13 (t, 1, AcOCH), 3.53 (t, 1, CH_3OCH), 3.30 (s, 3, OCH_3), 2.03 (s, 3, O_2CCH_3), and 2.4–1.3 ppm (6); mass spectrum (70 eV) *m/e* 182 (M^+). The major ester product was identified as *exo,exo*-3-acetoxy-5-carbomethoxynortricyclene (**5**) (64%): mp 33–34°; nmr ($CDCl_3$) δ 4.65 (t, 1, AcOCH), 3.65 (s, 3, CO_2CH_3), 2.56 (bs, 1, $HCCO_2CH_3$), 2.38 (bs, 1), 2.02 (s, 3, O_2CCH_3), and 1.9–1.3 ppm (5); mass spectrum (70 eV) *m/e* 210 (M^+). The minor ester product was identified as acetoxycarbomethoxynorbornene (**6**) (8%): nmr ($CDCl_3$) δ 6.26 (dd, 1, J = 6 Hz, 3.8 Hz), 5.92 (dd, 1, J = 6 Hz, 3 Hz), 4.41 (m, 1, AcOCH), 3.54 (s, 3, CO_2CH_3), 3.11 (m, 2), 2.81 (m, 2), 2.03 (s, 3, O_2CCH_3), 2.0 (m, 1), and 1.54 ppm (dd, 1, J = 12.5 Hz, 4 Hz); mass spectrum (70 eV) *m/e* 210 (M^+).

Carbonylation of *exo,exo*-3-Methoxynortricyclyl-5-mercuric Chloride (3). Carbonylation of a mixture of 2.0 g (5.6 mmol) of **3**,[10] 1.0 g (5.64 mmol) of palladium chloride, 0.5 g (11.8 mmol) of lithium chloride, and 1.0 g of sodium acetate in 100 ml of methanol in the manner described above afforded 0.7 g of organic products consisting of five components which were separated by preparative vpc using a 20 ft × ⅜ in. 30% DEGS/Chromosorb W column. Two of the components were identified as *exo,exo*-3-methoxy-5-

chloronortricyclene (**13x**) (31%) and *exo,endo*-3-methoxy-5-chloronortricyclene (**13n**) (18%), respectively, by nmr comparison with authentic samples.[16] A third nonester product was assigned the structure *exo,endo*-3,5-dimethoxynortricyclene (**14**) (5%): nmr ($CDCl_3$) δ 3.97 (bs, 1), 3.52 (t, 1), 3.30 (s, 6), and 2.2–1.2 ppm (6); mass spectrum (70 eV) *m/e* 154 (M^+). The major ester product was indentified as *exo,exo*-3-methoxy-5-carbomethoxynortricyclene (**11**) (34%) by vpc and nmr comparison with an authentic sample.[7] The minor ester product was identified as methoxycarbomethoxynortricyclene (**12**) (10%): nmr ($CDCl_3$) δ 6.10 (dd, 1, J = 6.1 Hz, 3.8 Hz), 5.88 (dd, 1, J = 6.1 Hz, 3.0 Hz), 3.62 (s, 3) 3.25 (s, 3), 3.3–2.6 (4), 1.87 (drn, 1, J = 12.5 Hz), and 1.44 ppm (dd, 1, J = 12.5 Hz, 3.8 Hz); mass spectrum (70 eV) *m/e* 183 (M^+).

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Registry No.—**1**, 5274-83-9; **2**, 32737-75-0; **3**, 53494-63-6; **4**, 13640-66-9; **5**, 53418-54-5; **6**, 53418-37-4; **8**, 53418-55-6; **9**, 53494-62-5; **10**, 53494-64-7; **12**, 53418-38-5; **14**, 53418-56-7; dichloro(norbornadiene)palladium(II), 12317-46-3; silver acetate, 563-63-3.

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A Stereochemical Study of the Mechanism of the Conversion of Phenyl(trichloromethyl)carbinol to α-Methoxyphenylacetic Acid[1]

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Two reaction pathways are considered for the reaction of phenyl(trichloromethyl)carbinol (**1**) with sodium methoxide to α-methoxyphenylacetic acid in methanol. Pathway 1 involves the conversion of the carbinol to a dichloro epoxide (**2**), followed by an SN2 attack of the methoxide nucleophile to give α-methoxyphenylacetic acid; this pathway involves one stereochemical inversion. The second pathway involves initial formation of the dichloro epoxide **2** followed by an intramolecular rearrangement to α-chlorophenylacetate anion and a subsequent attack of the methoxide nucleophile on this anion. This second pathway involves almost complete racemization during the 2-hr reaction period used; one step alone (**3** going to **4**) involves 96% racemization, and, in the next step, racemization of **4** occurs twice as fast as the conversion of **4** to **5**. The second pathway is proven to account for the formation of approximately 23% of the final product by the detection of the presence of 20% α-chlorophenylacetic acid in the crude α-methoxyphenylacetic acid and by measuring the kinetics of the reaction of the α-chloro acid with methoxide anion. The balance of the reaction proceeds by pathway 1 and this reaction pathway accounts for the stereochemistry experimentally observed. Nine per cent inversion of configuration occurs with the balance racemization. Control experiments show that the large amount of racemization is due to the ease with which α-methoxyphenylacetate anion racemizes in the methanolic potassium hydroxide reaction medium.

Phenyl(trichloromethyl)carbinol (**1**) reacts with a wide variety of nucleophiles at 50° in methanolic potassium hydroxide to form α-substituted phenylacetyl chlorides. These are not isolated but usually react with the basic solution to form α-substituted phenylacetate anions. Examples include reaction of the carbinol with methoxide to give α-methoxyphenylacetic acid[2] and with potassium amide in liquid ammonia to form α-aminophenylacetic acid.[3] With some nucleophiles ring closure occurs; thiourea forms 2-imino-5-phenyl-4-thiazolidinone,[4] and cyanamide forms alkyl 5-aryl-2-imino-4-oxo-1-imidazolidinecarboximidates.[5] All of these reactions occur in yields of 45–80% of the theoretical.

These reactions have been postulated to proceed through a dichloro epoxide (**2**) followed by an SN2 attack of the nucleophile on this epoxide. This seems inherently reasonable because it is necessary to rationalize somehow the facile substitution of the α-hydroxyl group of the starting carbinol by the new nucleophile, and it is well-known that hydroxyl groups themselves are very poor leaving groups in SN2 reactions. The hydroxyl group of phenyl(trichloromethyl)carbinol is even more inert than the hydroxyl group of a typical secondary alcohol; it does not react with Lucas reagent (concentrated hydrochloric acid containing zinc chloride), either under the usual room-temperature conditions or after standing at steam bath temperature for 90 min.

An alternative mechanism involves the dichloro epoxide intermediate first rearranging to the α-chlorophenylacetyl chloride, which then hydrolyzes and reacts with the nucleophile. Phenyl(trichloromethyl)carbinol is known to be slowly converted to α-chlorophenylacetic acid in 27% yield by 10% aqueous potassium hydroxide at 0°.[6] We have found the half-life for this reaction to be 16 hr at 0° under heterogeneous, aqueous reaction conditions. These experimental conditions are quite different from those employed