dried in vacuo. The total yield was 5.4 g (74% yield based on starting phosphine). Anal. Calcd for $C_{39}H_{42}P_3F_6Rh$: C, 57.09; H, 5.16; P, 11.32. Found: C, 56.63; H, 5.40; P, 11.01.

**(E) Hydrogenation Procedure.** All solvents used for the hydrogenations were dried and degassed prior to use. In all cases the procedure involved loading the weighed substrate (~2 g) and catalyst precursor, [Rh((*R*)-Cycphos)(NBD)]$PF_6$, into a dimpled flask which was transferred to an inert-atmosphere glovebox. To the flask was added the desired amount of solvent (generally 30 mL). The flask (sealed via a stopcock) was then transferred to the hydrogenation line. After several pump/purge cycles, the hydrogenations were begun via vigorous shaking. Reactions were allowed to go to completion via monitoring the $H_2$ uptake.

The workup of an acid product was carried out by removing all the solvent on a rotary evaporator and then dissolving the residue in $CH_2Cl_2$ or other suitable (non-water-miscible) solvent. The organic layer was then extracted once with 1 N NaOH solution. The organic phase that contains the catalyst residues can be discarded. The organic layer was filtered to remove any suspended material and then acidified with concentrated HCl. The water layer was then extracted with $Et_2O$ or other suitable organic solvent, and this organic layer was then dried over $Na_2SO_4$. Filtration followed by removal of all solvent afforded solid (generally crystalline) products which were then weighed directly to obtain optical rotations and also $^1H$ NMR spectra. For some of the acids (*N*-acetylalanine and *N*-acetyltyrosine) which are $H_2O$ soluble, the neutralization step is followed by removal of all $H_2O$. The solid residue is then extracted with an organic solvent (EtOAc) to dissolve the product and leave the NaCl behind.

For esters and alcohol products, the catalyst removal was effected by silica gel chromatography using 30% EtOAc in hexanes as the eluent.

**Acknowledgment.** We thank Dr. Douglas Hager for many useful discussions.

**Registry No.** (*S*)-Mandelic acid, 17199-29-0; (*S*)-hexahydromandelic acid, 61475-31-8; (*S*)-cyclohexyl-1,2-ethanediol, 61414-09-3; (*S*)-cyclohexyl-1,2-bis(*p*-toluenesulfonyloxy)ethane, 75421-30-6; (*R*)-cycphos, 75421-31-7; L-2-amino-5-methylhexanoic acid, 31872-98-7; L-leucine, 61-90-5; L-phenylalanine, 63-91-2; L-tyrosine, 60-18-4; L-tryptophan, 73-22-3; L-alanine, 56-41-7; hydratropic acid, 492-37-5; 1-phenylethanol, 98-85-1; lactic acid, 50-21-5; L-valine, 72-18-4; (*Z*)-2-benzamido-5-methyl-2-hexenoic acid, 75421-32-8; methyl (*Z*)-2-benzamido-5-methyl-2-hexenoate, 75421-33-9; (*Z*)-2-benzamido-4-methyl-2-pentenoic acid, 64896-31-7; (*Z*)-2-benzamido-3-phenyl-2-propenoic acid, 26348-47-0; ethyl (*Z*)-2-benzamido-3-phenyl-2-propenoate, 26348-46-9; (*Z*)-2-acetamido-3-phenyl-2-propenoic acid, 55065-02-6; (*Z*)-2-benzamido-3-(*p*-hydroxyphenyl)-2-propenoic acid, 64896-32-8; (*Z*)-2-acetamido-3-(*p*-hydroxyphenyl)-2-propenoic acid, 64896-33-9; (*Z*)-2-acetamido-3-(3-indolyl)-2-propenoic acid, 70082-70-1; 2-acetamidopropenoic acid, 5429-56-1; 2-phenylpropenoic acid, 492-38-6; 1-phenylethanone, 98-86-2; methyl 2-oxopropanoate, 600-22-6; 2-benzamido-3-phenyl-2-butanoic acid, 1738-64-3; (*R*)-prophos, 67884-32-6; L-2-benzamido-5-methylhexanoic acid, 75421-34-0; methyl L-2-benzamido-5-methylhexanoate, 75421-35-1; Ni(cycphos)$_2$ thiocyanate complex, 75421-74-8; [Rh((*R*)-cycphos)(NBD)]$PF_6$, 75421-76-0; $(Rh(NBD)Cl)_2$, 12257-42-0.

# Cyclopropanation of Ester Enolates by π-Allylpalladium Chloride Complexes

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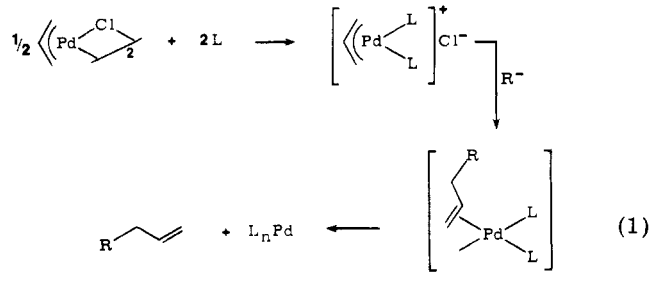
Branched ester enolates react with π-allylpalladium chloride complexes in the presence of $Et_3N$ and HMPA to produce alkylated cyclopropanes. Labeling studies indicate the carbanion attacks the *central* carbon of the π-allyl complex.

## Introduction

The reaction of π-allylpalladium halide complexes with stabilized carbanions in the presence of excess phosphine or in polar aprotic solvents such as $Me_2SO$ results in allylic alkylation (eq 1).[1] With unsymmetrical π-allylpalladium



(1)

complexes, attack occurs at either or both of the terminal allylic carbons, depending on the specific carbanion and π-allylpalladium complex.[1c] This chemistry has found extensive application in organic synthesis and both inter-[2] and intramolecular[3] processes have been developed.

The generally accepted mechanism for this reaction involves external (without prior coordination) nucleophilic attack on a cationic π-allylpalladium complex generated by displacement of chloride by added ligand (or solvent) (eq 1).[1c,4,5] The limitation of this reaction to relatively stabilized ($pK_a < \sim 17$) anions may be due to the propensity of nonstabilized carbanions to attack the *metal* in preference to the allyl group,[6,7] resulting in reduction of the complex rather than alkylation. This restriction to stabilized carbanions is fairly general throughout organopalladium chemistry. Initially the palladium assisted al-

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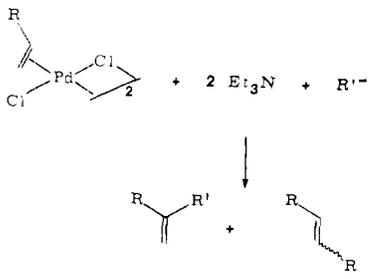
kylation of olefins (eq 2) was also restricted to stabilized



(2)

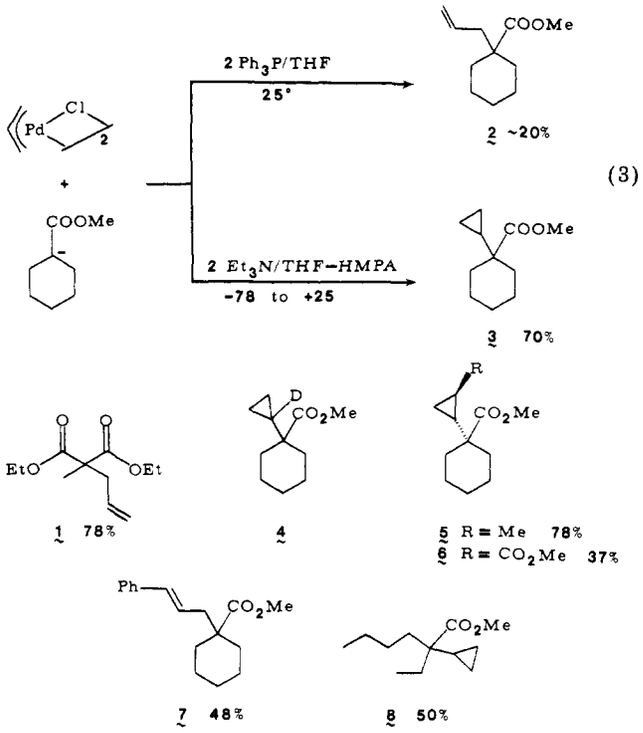
carbanions.[8] Nonstabilized carbanions rapidly reduced Pd(II) to Pd(0), without alkylating the olefin. However, addition of HMPA [$(Me_2N)_3PO$] to this reaction completely suppressed reduction and permitted the alkylation to proceed with nonstabilized carbanions as well.[9] This successful extension of the olefin alkylation reaction to nonstabilized carbanions led us to try a similar approach to the alkylation of $\pi$-allylpalladium chloride complexes with nonstabilized carbanions.

## Results and Discussion

For confirmation that the use of HMPA and $Et_3N$ as ligands did not interfere with the allylation of *stabilized* carbanions, $\pi$-allylpalladium chloride in THF was treated with 20 equiv of HMPA, cooled to −78 °C, and then treated with 2 equiv of $Et_3N$ and 1 equiv of the enolate of diethyl methylmalonate (typical *olefin* alkylation procedures[9]). After the mixture was warmed to 25 °C and routine isolation, the allyl malonate 1 was obtained in reasonable yield. Thus HMPA/$Et_3N$ could replace $Ph_3P$ in these reactions of stabilized carbanions. In the olefin alkylation reaction (eq 2) the enolate of methyl cyclohexanecarboxylate failed to alkylate olefins in the absence of HMPA but reacted cleanly in the presence of HMPA.[9] Treatment of $\pi$-allylpalladium chloride with the enolate of methyl cyclohexanecarboxylate under standard conditions ($Ph_3P$/THF, 25 °C, 16 h) led to very low yields of allyl product 2. Repeating the reaction under olefin alkylation conditions (THF/HMPA/$Et_3N$, −60 to +25 °C) led to *excellent yields of cyclopropane* 3 (eq 3). When the reaction was carried out with 2-deuterio-$\pi$-allylpalladium chloride, the deuterium appeared exclusively at the alkylated position of the cyclopropane (4), indicating that nucleophilic attack had occurred on the *central* carbon of the $\pi$-allyl ligand.

This cyclopropanation reaction was not restricted to this simple case. $\pi$-Allylpalladium complexes having a methyl or a carbomethoxy group at the one position also reacted to give the 1,2-disubstituted cyclopropanes 5 and 6. In contrast, the $\pi$-(1-phenylallyl)palladium complex reacted to give exclusively the allylic alkylation product 7, with no cyclopropane products being detected. The $\pi$-(2-methylallyl)-, $\pi$-(1,3-dimethylallyl)-, and $\pi$-cycloheptenylpalladium chloride complexes failed to undergo alkylation under the above conditions, although they were consumed in some unspecified fashion.

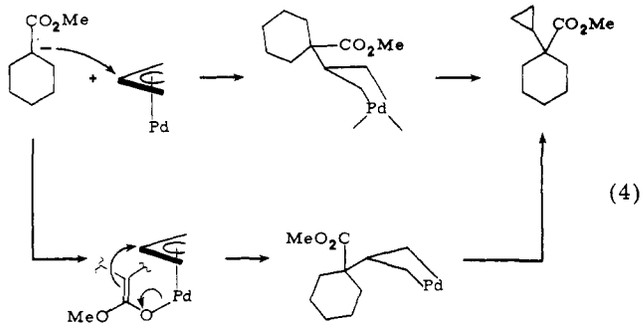
Branched ester enolates were the only carbanions studied that led to cyclopropanation. Thus, the enolate of methyl 2-ethylhexanoate produced cyclopropane 8 in fair yield. In contrast, the anions of methyl hexanoate, acetophenone, 2-cyanopropane, cyclohexanone enamine and acetophenone enamine failed to produce material containing the $\pi$-allyl fragment *in any form*, although the



(3)

$\pi$-allylpalladium complex was consumed.

A reasonable mechanism for cyclopropanation involves direct nucleophilic attack on the central carbon of the $\pi$-allyl system to form a palladiacyclobutane, followed by reductive elimination to produce the cyclopropane and the observed Pd(0). Alternatively, attack at palladium could occur followed by transfer to the $\pi$-allyl ligand (eq 4).



(4)

Direct attack by nucleophiles at the central carbon of a $\pi$-allyl complex has been observed in the reactions of both $[W(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}CH_2CHCH_2)]^+$ and the Mo analogue with methyllithium or sodium borohydride.[10,11] In these cases, stable metallacyclobutanes were isolated and characterized. Exclusive attack at the central carbon of these $\pi$-allyl systems was consistent with earlier observations[12] that electron-rich, cationic, 18-electron compounds reacted with nucleophiles to retain the valence state of the metal. For $\pi$-allylpalladium complexes to meet these criteria, 3 equiv of HMPA and/or $Et_3N$ would have to coordinate to the metal, forming [$\pi$-allyl $PdL_3$]$^+$ species.

The reaction may also occur by initial attack of the carbanion at the metal followed by intramolecular transfer to the $\pi$-allyl group. Ester enolates can metalate at oxygen then alkylate at carbon. Nonstabilized carbanions have

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been claimed to prefer to attack at palladium rather than at a complexed ligand.[6,7] Further, it has been demonstrated that HMPA stabilizes olefin–palladium(II) complexes toward reduction by nonstabilized carbanions.[9]

Both proposed routes involve a palladiacyclobutane as an intermediate. Efforts to trap this metallacycle with carbon monoxide to produce carbonylated products failed. Instead, exposure of the reaction mixture to carbon monoxide after addition of all other reactants either had no effect or in some cases slightly increased the yield of cyclopropanation. Other mechanisms not involving direct attack of carbanion at the central carbon of the allyl group can be written. However, they are somewhat more complex and are not warranted by the currently available data.

## Experimental Section

**General.** Infrared spectra were recorded on a Beckman 2440 spectrophotometer and are reported in $cm^{-1}$. $^1H$ NMR spectra were measured with either a Varian EM-360, JEOL FX 100, Nicolet 150, or Nicolet 360 MHz instrument, using $Me_4Si$ as internal standard, and are reported in $\delta$ units. $^{13}C$ NMR spectra were recorded on a JEOL FX100 instrument.

Analytical and preparative vapor-phase chromatography were performed on a Bendix Model 2300 gas chromatograph equipped with a 10 ft × 0.25 in. SE-30 10% on Chromosorb W NAW 60–80-mesh column and a thermal-conductivity detector.

**Materials.** Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone and was degassed with argon prior to use. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride under reduced pressure. The remaining chemicals were commercially available and were used without additional purification.

**Preparation of $\pi$-Allylpalladium Chloride Complexes.** $\pi$-Allylpalladium chloride, $\pi$-(1-methylallyl)palladium chloride, $\pi$-(2-methylallyl)palladium chloride, $\pi$-(2-deuterioallyl)palladium chloride, and $\pi$-(1-phenylallyl)palladium chloride were prepared from the corresponding allylic chlorides by literature methods.[13] $\pi$-(1,3-Dimethylallyl)palladium chloride and $\pi$-[(1,3-tetramethylene)allyl]palladium chloride were prepared from 2-pentene and cycloheptene, respectively.[14] $\pi$-[1-(Carbomethoxy)allyl]-palladium chloride was prepared from methyl crotonate.[15]

**Preparation of $\pi$-(2-Deuterioallyl)palladium Chloride.** The Diels–Alder adduct of anthracene and methyl acrylate was prepared by the method of Bartlett and Tate.[16] This adduct (47 g, 0.18 mol) in 250 mL of THF was treated with 0.27 mol of LDA (from 38 mL of diisopropylamine and 100 mL of 2.70 M *n*-butyllithium) at −20 °C for 16 h. The dark brown solution was quenched by the addition of 10 mL of $D_2O$. Removal of solvent and recrystallization from diethyl ether/petroleum ether gave 41 g (86%) of a white crystalline solid. The extent of deuteration was ~60% by NMR integration.[17] The deuterated adduct (40 g, 0.15 mol) was reduced by the method of Bartlett[16] to produce 34 g (95%) of the corresponding alcohol. Retro-Diels–Alder reaction[16] produced 5.6 g (66%) of the pure allyl alcohol (bp 93 °C). The material was 64% deuterated by NMR integration. Deuterated allyl alcohol (1.51 g, 0.026 mol) was placed in a 10-mL flask fitted with a condenser, and thionyl chloride (1.86 mL, 0.026 mol) was carefully added. The resulting mixture was stirred for 10 min at 25 °C. This material in 1 mL of water was added to a solution of palladium chloride (1.05 g, 6 mmol) and sodium chloride (0.75 g, 13 mmol) in 40 mL of methanol that had been stirred for 16 h at 25 °C. The mixture was stirred under an atmosphere of carbon monoxide for 1 h and partitioned between chloroform and water. The chloroform solution was dried over magnesium sulfate and evaporated to dryness, leaving a yellow, crystalline solid (0.77 g, 70%). The NMR spectrum ($CDCl_3$/$Me_4Si$) of this material consisted of a singlet at $\delta$ 3.08 (anti H's) and a singlet at $\delta$ 4.18 (syn H's). Each of these singlets, due to the deuterated $\pi$-allyl group, was flanked by the doublets from the same protons of the nondeuterated complex. The central proton of nondeuterated material appeared as a multiplet centered at $\delta$ 5.5. The complex was 60% deuterated by NMR.

**General Procedure for Preparation of Ester Enolates.** A 25-mL 14/40 Airlessware flask with a stirring bar was dried in an oven, fitted with a serum cap, degassed, and filled with argon. An argon-filled balloon was attached to the side arm, and 10 mL of THF and the appropriate amount of diisopropylamine were added. The solution was cooled to 0 °C, and 1 equiv of *n*-BuLi was added. The LDA solution was stirred ~5 min and then cooled to −78 °C. Ester (1 equiv) was added, and the reaction was then stirred at −78 °C for 10 min, 0 °C for 10 min, and −78 °C until needed (0.5–1 h). The anion solution was added to the substrate via a precooled, degassed syringe.

**General Cyclopropanation Reaction.** The $\pi$-allylpalladium chloride complex (0.55 mmol) was placed in a 50-mL Airlessware flask fitted with a stirring bar and a serum cap. The flask was repeatedly evacuated and filled with argon (3–4 times). An argon filled balloon was attached and 10 mL of THF was added, giving a yellow solution. HMPA (3 mL) was then added and the reaction was cooled to −78 °C. The $NEt_3$ (0.3 mL) was added dropwise over ~10 min. After the mixture was stirred for 10–20 min, the anion solution (2.2 mmol) was added, causing the reaction to turn deep brown within 5 min. In some cases a CO balloon was attached, and the reaction was allowed to warm to room temperature overnight. When the reaction had turned black, the solvent was removed, and the reaction mixture was taken up in ether (~150 mL), filtered, and washed with water (3 × 70 mL). The aqueous layer was back extracted with ether, the combined ether layers were washed with saturated NaCl solution, dried over magnesium sulfate, and filtered, and the ether was removed on the rotary evaporator to yield the product as a crude oil.

**Product Purification and Characterization. A. Diethyl Methylallylmalonate (1).** By use of 0.2 g (0.55 mmol) of $\pi$-allylpalladium chloride, 0.38 g (2.2 mmol) of diethyl methylmalonate, and 2.2 mmol LDA, 0.18 g (78%) of compound 1 was obtained after purification by standard procedures.[9] It was identical in all respects with material prepared by the reaction of the sodium salt of diethyl methylmalonate with allyl bromide.

**B. 1-(Carbomethoxy)-1-cyclopropylcyclohexane (3).** From 0.2 g (0.55 mmol) of $\pi$-allylpalladium chloride, 0.31 g (2.2 mmol) of methyl cyclohexanecarboxylate, and 2.2 mmol of LDA, 0.14 g (70%) of compound 3 was obtained after purification by preparative-layer chromatography (silica gel, 8:1 hexane/ether, $R_f$ 0.70); $^1H$ NMR (150 MHz, $CDCl_3/Me_4Si$) $\delta$ 0.317 (apparent d, $J$ = 7 Hz, 4, cyclopropyl-$CH_2CH_2$), 0.89 (apparent quintet, 1, cyclopropyl-CH), 1.08–1.40, 1.58–1.61, 1.98–2.05 (m's, 10, cyclohexyl-$CH_2$), 3.68 (s, 3, $OCH_3$). Assignments were made by complete spin decoupling. Irradiation of the $\delta$ 0.317 doublet led to collapse of the $\delta$ 0.89 quintet to a singlet. Irradiation of this quintet caused the $\delta$ 0.317 doublet to collapse to a singlet:[18] $^{13}C$ NMR ($CCl_4/Me_4Si$) $\delta$ −1.702 (t, cyclopropyl-$CH_2CH_2$), 18.31 (d, cyclopropyl CH), 21.01 (t, cyclohexyl $\gamma$-$CH_2$-'s), 23.39 (t, cyclohexyl $\delta$-$CH_2$), 30.20 (t, cyclohexyl $\alpha$-$CH_2$-'s), 44.18 (s, cyclohexyl quaternary C), 48.31 (q, $OCH_3$), 171.67 (s, CO); IR ($CCl_4$) 1722 $cm^{-1}$ (C=O). Anal. ($C_{11}H_{18}O_2$) C, H.

**C. 1-(Carbomethoxy)-1-(1-deuteriocyclopropyl)cyclohexane (4).** This reaction was run exactly as in method B. The $^1H$ NMR spectrum was identical with that of the nondeuterated material 3, except the doublet centered at $\delta$ 0.317 collapsed to a singlet at the same position. Since the deuterated product contained some nondeuterated material, a residual multiplet, much reduced in intensity, was observed at $\delta$ 0.89, as was a residual doublet centered at $\delta$ 0.317.

**D. 1-(Carbomethoxy)-1-(2-methylcyclopropyl)cyclohexane (5).** Use of 0.22 g (0.55 mmol) of $\pi$-crotylpalladium chloride led to production of 0.17 g (78%) of compound 5 after purification by preparative-layer chromatography (silica gel, 8:1 hexane/ether, $R_f$ 0.6); $^1H$ NMR (360 MHz, benzene-$d_6$/$Me_4Si$) $\delta$ −0.24 (ddd, 1, cyclopropyl CH, $J_{CHCH}$ = 4.7 Hz (trans), $J_{CH-CH_2}$ = 7.2, 10.8 Hz),

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(16) P. D. Bartlett and F. A. Tate, *J. Am. Chem. Soc.*, **75**, 91 (1953).
(17) R. K. Hill and G. R. Newcombe, *J. Org. Chem.*, **34**, 740 (1969).
(18) At 360 MHz, in benzene-$d_6$, compound 3 exhibited a multiplet at $\delta$ 0.208 and a multiplet at $\delta$ 0.355 for the cyclopropyl $CH_2$'s, and a triplet of triplets at $\delta$ 0.81 ($J$ = 9.0 and 5.7 Hz) for the cyclopropyl CH group.

+0.28 (m, 2, cyclopropyl $CH_2$), 0.47 (m, 1, cyclopropyl $CH_3CH$), 0.65 (d, 3, $J$ = 5.9 Hz, $CH_3$), 0.80, 1.15, 1.35, 1.85 (m's, 10, cyclohexyl $CH_2$'s), 3.30 (s, 3, $OCH_3$). Trans stereochemistry was assigned to this compound because of the 4.7-Hz coupling constant, which is too small to be due to cis coupling;[19] IR ($CCl_4$) 1740 $cm^{-1}$ (C=O). Anal. ($C_{12}H_{20}O_2$) C, H.

**E. 1-(Carbomethoxy)-1-(2-(carbomethoxy)cyclopropyl)-cyclohexane (6).** Use of 0.27 g (0.55 mmol) of $\pi$-[1-(carbomethoxy)allyl]palladium chloride produced 0.098 g (37%) of compound 6 after purification by preparative-layer chromatography (silica gel, 2:1 hexane/ether, $R_f$ 0.4): $^1H$ NMR (360 MHz, benzene-$d_6$/$Me_4Si$) $\delta$ 0.77 (apparent 8-line m, 1, cyclopropyl CH), 0.92, 1.30, 1.45, 2.08 (m's, 10, cyclohexyl $CH_2$'s), 1.13 (m, 1, 1 H of cyclopropyl $CH_2$), 1.73 (m, 2, cyclopropyl CHCOOMe and other H of $CH_2$), 3.24 (s, 3, $OCH_3$), 3.36 (s, 3, $OCH_3$); $^{13}C$ NMR (benzene-$d_6$/$Me_4Si$) $\delta$ 11.44 (t, cyclopropyl $CH_2$), 16.52 (d, cyclopropyl CH), 23.70 (m, cyclohexyl $C_3$ and $C_5$), 25.81 (m, cyclohexyl $C_4$), 31.29 (d, cyclopropyl CHCOOMe), 33.16 (t, cyclohexyl $C_2$ and $C_6$), 46.53 (s, cyclohexyl quaternary $C_1$), 51.09 (q, $CH_3O$), 51.26 (q, $CH_3O$), 173.59 (s, C=O), 174.34 (s, C=O); IR ($CCl_4$) 1728 $cm^{-1}$ (C=O). Anal. ($C_{13}H_{20}O_4$) C, H.

**F. 1-(Carbomethoxy)-1-(3-phenyl-2-propenyl)cyclohexane (7).** From 0.29 g (0.55 mmol) of $\pi$-(1-phenylallyl)palladium chloride, 0.14 g (48%) of compound 7 was obtained after purification by preparative-layer chromatography (silica gel, 2:1 hexane/ether, $R_f$ 0.4): $^1H$ NMR ($CCl_4$/$Me_4Si$) $\delta$ 1.3, 2.1 (br m's, 10, cyclohexyl $CH_2$'s), 2.33 (t, $J$ = 6 Hz, 2, $CH_2C$=), 3.60 (s, 3, $OCH_3$), 6.1 (m, 2, CH=CH), 7.2 (m, 5, Ar H); IR ($CCl_4$) 1735 $cm^{-1}$ (C=O). This material is identical in all respects with that made by the alkylation of cinnamyl bromide with the enolate of methyl cyclohexanecarboxylate.

**G. Methyl 2-Ethyl-2-cyclopropylhexanoate (8).** By use of 0.20 g (0.55 mmol) of $\pi$-allylpalladium chloride and 0.35 g (2.2 mmol) of methyl 2-ethylhexanoate, compound 8 (0.11 g, 50%) was obtained after purification by preparative-layer chromatography (silica gel, 4:1 hexane/ether, $R_f$ 0.8): $^1H$ NMR (360 MHz, $CDCl_3$/$Me_4Si$) $\delta$ 0.32 (m, 4, cyclopropyl $CH_2CH_2$), 0.86 (t, 3, $J$ = 7.2 Hz, $CH_3$), 0.91 (t, 3, $J$ = 7.2 Hz, $CH_3$), 1.18 (m, 1, cyclopropyl CH), 1.3, 1.5 (m's, 6, $CH_2$'s), 1.57 (q, 2, $J$ = 7.3 Hz, $CCH_2CH_3$), 3.63 (s, 3, $OCH_3$); IR ($CCl_4$) 1725 $cm^{-1}$ (C=O). Anal. ($C_{12}H_{22}O_2$) C, H.

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**Registry No.** 1, 53651-72-2; 3, 75266-48-7; 4, 75266-48-7; 5, 75266-49-8; 6, 75266-50-1; 7, 75266-51-2; 8, 75266-52-3; $\pi$-(2-deuterioallyl)palladium chloride, 75284-17-2; diethyl methylmalonate, 609-08-5; $\pi$-allylpalladium chloride, 12012-95-2; methyl cyclohexanecarboxylate, 4630-82-4; $\pi$-crotylpalladium chloride, 12081-22-0; $\pi$-[1-(carbomethoxy)allyl]palladium chloride, 12117-04-3; $\pi$-(1-phenylallyl)palladium chloride, 12131-44-1; methyl 2-ethylhexanoate, 816-19-3.

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# Reactions of Protoporphyrin with Tetracyanoethylene

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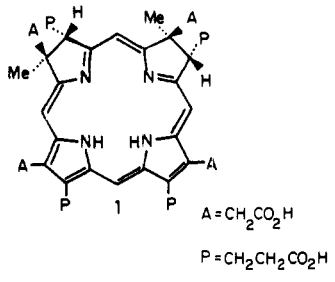
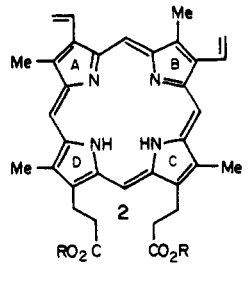
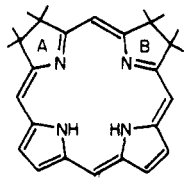
The vinyl groups of protoporphyrin react with tetracyanoethylene (TCNE) in a [2 + 2] reaction to give adducts containing one and two cyclobutane rings. In addition, the vinyl groups and the porphyrinic $\beta$-$\beta$ cross-conjugated double bonds in rings A and B react with TCNE in a [4 + 2] cycloaddition reaction, giving chlorins when either ring A or B reacts or an isobacteriochlorin when both rings react. Reactions in which one vinyl group reacted in a [2 + 2] and the other in a [4 + 2] fashion were also observed.

The recent appreciation of the role of sirohydrochlorin (1) in the biosynthesis of vitamin $B_{12}$[1] and that of siroheme (the iron complex of 1) in the enzymatic reduction of nitrite and sulfite[2] has highlighted the importance of the isobacteriochlorin chromophore in nature.

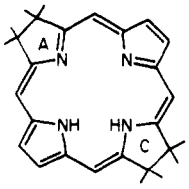



Isobacteriochlorins (3), in which the $\beta$-$\beta'$ cross-conjugated double bonds in rings A and B of the porphyrin nucleus have been reduced, can be prepared from the reduction of porphyrins under a variety of reducing conditions.[3] Reduction of metalloporphyrins with sodium in amyl alcohol[4] increases the yield of the isobacteriochlorin over that of bacteriochlorin (4) where the cross conjugated




isobacteriochlorin 3




bacteriochlorin 4

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