relieves the strain at the C-4 position[10-12] imposed by the bromine atom.

The tendency of the molecule to part from the bromine atom at C-4 is also reflected by the facile dehydrobromination of 4β-bromo ketone **2** as compared to 2β-bromo isomer **3**.

Another noteworthy observation is that the bromination of **1** to produce 4β-bromo ketone **2** is much slower with IBr (2 hr) than with Br_2 (5 min). Moreover, the slow rate of the monobromination with IBr did not change appreciably when 1, or even 2, equiv of Br_2 was added to the reaction mixture, implying that in the presence of IBr enolization is depressed. This peculiar behavior could be a result of molecular compound formation between the 3-keto substrate and iodine monobromide.[14-18] The coordinated IBr molecule would then interfere in the process of enolization initiated by the protonation at the oxygen carbonyl group.

The introduction of bromine at C-2 in methyl 3-oxo-5β-cholanate (**1**) is significant, since it is the first reported case in which heterolytic bromination of **1** takes place exclusively at a site unfavorable for enolization.

Experimental Section

Ultraviolet spectra were determined with a Unicam ultraviolet spectrophotometer (Model Sp 300A). Infrared spectra were measured in potassium bromide disks using a Perkin-Elmer spectrophotometer (Model 337). Nmr spectra were recorded on a Jeol C-60-H high-resolution nmr spectrometer with tetramethylsilane as internal standard. CD spectra were obtained using a Cary 60 recording spectropolarimeter. Optical rotations were determined with a Perkin-Elmer 141 polarimeter. Mass spectra were recorded on a CH5 Varian MAT mass spectrometer. IBr was prepared by dissolving 1 g of iodine and 0.614 g of bromine in 50 ml of glacial acetic acid (1 mmol of IBr per 6.35 ml). Column chromatography and tlc were carried out on silica gel (Hopkins and Williams) and Kieselgel GF 254 from Stahl Merck, respectively.

Methyl 3-Oxo-5β-cholanate (1) was prepared according to the procedure of Fieser and Ettorre:[19] mp 119° (lit.[19] mp 119–120°); ir 1706 cm^{-1} (C=O); uv (ethanol) 285 nm (ε 19); nmr ($CDCl_3$) δ 0.70 (s, 3, 18-CH_3), 1.03 (s, 3, 19-CH_3), 3.68 (s, 3, 24-OCH_3); CD (ethanol) $[\theta]_{262}$ 0, $[\theta]_{285}$ −1600, $[\theta]_{318}$ 0; mass spectrum *m/e* (rel intensity) 388 (base peak, M^+), 537 (52, M − 31), 275 (93).

Bromination of 1 with IBr for 2 Hr. To a solution of **1** (388 mg) in acetic acid (10 ml) 2 equiv of IBr (12.7 ml) was added. After standing for 2 hr at room temperature the reaction mixture was diluted with water (100 ml) and sufficient sodium bisulfite was added. The precipitate was filtered, washed with water, and dissolved in chloroform. The solvent was removed and the solid residue was crystallized from methanol to yield pure 4β-bromo ketone **2**: mp 100–100.5° (lit.[3] mp 96–101°); $[\alpha]_D$ ($CHCl_3$) +51.0°; ir 1725 (C=O), 710–700 cm^{-1} (C–Br); uv (ethanol) 280 nm (ε 25); nmr ($CDCl_3$) δ 0.70 (s, 3, 18-CH_3), 1.09 (s, 3, 19-CH_3), 3.67 (s, 3, 24-OCH_3), 4.90 and 5.07 (d, 1, H–C–Br); CD (ethanol) $[\theta]_{250}$ 0, $[\theta]_{282}$ −660, $[\theta]_{300}$ 0, $[\theta]_{310}$ +240, $[\theta]_{330}$ 0; mass spectrum *m/e* (rel intensity) 468, 466 (0, M^+), 355 [base peak, M − (HBr + 31)], 419, 417 (9, M − 49), 387 (60, M − Br), 369 [33, M − (HBr + H_2O)], 337 (33), 55 (66, CH_2=CHC≡O^+).

Anal. Calcd: C, 64.24; H, 8.35; Br, 17.13. Found: C, 64.10; H, 8.25; Br, 17.16.

Bromination of 1 with Br_2 in the Presence of IBr. To a solution of **1** (388 mg) in acetic acid (10 ml), 1 equiv of IBr (6.4 ml) and 1 equiv of Br_2 were added. The product which was isolated after 2 hr by the above procedure proved to be identical in all respects with 4β-bromo ketone **2**. The same result was also obtained when **1** was subjected to the action of 2 equiv of Br_2 in the presence of 1 equiv of IBr under the same conditions.

Methyl 2β-Bromo-3-oxocholanate (3). To a solution of methyl 3-oxo-5β-cholanate (**1**, 500 mg) in acetic acid (10 ml), 2 equiv of IBr solution (16.4 ml) and 2 drops of 10% HBr in acetic acid were added and the reaction mixture was kept for 5 days at 30°. The brown residue which was obtained after the usual work-up was chromatographed and purified by plc (8% acetic acid in benzene). Recrystallization from methanol yielded 300 mg of pure methyl 2β-bromo-3-oxocholanate (**3**): mp 85°; $[\alpha]_D$ ($CHCl_3$) +2.4°; ir 1730 (C=O), 702 cm^{-1} (C–Br); uv (ethanol) 280 nm (ε 25); nmr ($CDCl_3$) δ 0.70 (s, 3, 18-CH_3), 1.07 (s, 3, 19-CH_3), 3.7 (s, 3, 24-OCH_3), 4.57, 4.66, 4.80, and 4.88 (q, 1, H–C–Br); CD (ethanol) $[\theta]_{258}$ 0, $[\theta]_{287}$ −1600, $[\theta]_{332}$ 0; mass spectrum *m/e* (rel intensity) 468, 466 (0, M^+), 355 (base peak), 419, 417 (13), 387 (85), 369 (47), 337 (53), 55 (91).

Anal. Calcd: C, 64.24; H, 8.35; Br, 17.13. Found: C, 64.04; H, 8.17; Br, 17.37.

Table I
Formation of 2β-Bromo Ketone 3

Time, hr	Height of peak at δ 1.07/ height of peak at δ 1.09
12	~0.1
36	~1.2
60	~20
84	~30
120	No peaks at δ 1.09 and 5.07

Bromination of 1 with IBr at Different Intervals of Time. To a solution of **1** (388 mg) in acetic acid (10 ml) 2 equiv of IBr (12.7 ml) and 2 drops of 10% HBr were added and the reaction mixture was kept at 30°. Aliquots of 4 ml were taken after 12, 36, 60, 84, and 120 hr and analyzed by nmr after the usual work-up. The formation of 2β-bromo ketone **3** was followed by the appearance of the peaks at δ 1.07, 4.57, 4.66, 4.80, and 4.88. The results are summarized in Table I.

Rearrangement of 2 to 3. To a solution of 4β-bromo ketone **2** (467 mg) and I_2 (254 mg) in acetic acid (10 ml), 2 drops of 10% HBr in acetic acid was added. The reaction mixture was kept at 30°. Aliquots of 2 ml were taken after 12, 36, 60, 84, and 120 hr and analyzed by nmr. The results were similar to those represented in Table I for the formation of 2β-bromo ketone **3** by the action of iodine monobromide on **1**.

The rearrangement with I_2 was not complete after 5 days in the absence of HBr. HBr alone was found to be ineffective.

Registry No.—**1**, 1173-32-6; **2**, 52032-49-2; **3**, 52032-50-5; IBr, 7789-33-5.

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Synthesis of Methyloxocyclopentaneacetic Acids

Mario Giannella, Fulvio Gualtieri,* and Carlo Melchiorre

Institute of Organic and Pharmaceutical Chemistry, University of Camerino, Camerino, Italy

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In studying the synthesis of a carbocyclic analog of muscarone,[1] 4-methyl-3-oxo-1-cyclopentaneacetic acid was required. An attempt was made to synthesize it by a Wittig reaction between 4-methyl-4-cyclopentene-1,3-dione[2] and triphenylcarbethoxymethylenephosphorane[3] using benzoic acid as catalyst.[4] Contrary to reports[5,6] on similar experiments, the reaction took place under mild conditions, yielding ethyl 3-methyl-4-oxo-2-cyclopenten-1-ylideneace-

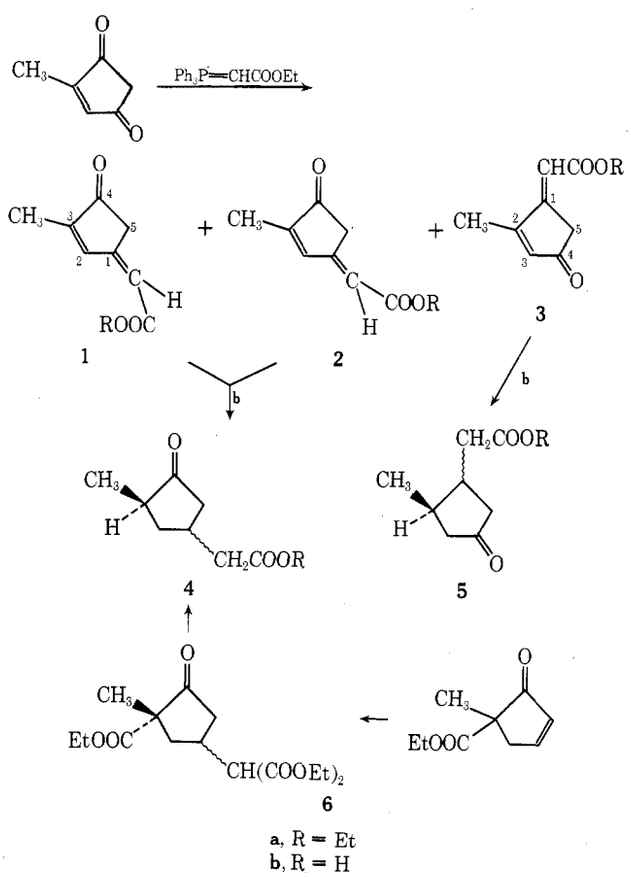
tate (**1a** and **2a**) and 2-methyl-4-oxo-2-cyclopenten-1-ylideneacetate (**3a**) in a 1:1.8 ratio.

The products were isolated by column chromatography and the isomers were identified by their nmr spectra. The C-2 proton in **1a** and **2a** absorbed at lower fields than the C-3 proton in isomer **3a**, consistent with the former being a vinylic proton β to a keto group. Furthermore, the anisotropic effect of the ester group causes a downfield shift of the C-2 proton in the *Z* form, allowing the distinction of the two isomers **1a** and **2a**. It is interesting to note that the nmr spectrum of **2a** showed $J \cong 1.5$ Hz for allylic coupling between the proton α to the ester group and the two protons of C-5. In compound **1a**, the same coupling was definitely smaller in that it resulted in simply a broadening of the C-5 proton signal. This confirms Newsoroff's observations[7] on *J* cisoid and *J* transoid (*J* cisoid < *J* transoid) constants.

Catalytic reduction of **1a**, **2a**, and **3a** led to the esters **4a** and **5a**, which were easily hydrolyzed to the corresponding acids **4b** and **5b**. The nmr spectra showed that compound **5** was a 60:40 mixture of cis and trans isomers.

To avoid obtaining several isomers simultaneously and to verify the assignment of the structures, 3-methyl-4-oxo-1-cyclopentaneacetic acid was also synthesized starting from ethyl 1-methyl-2-oxo-3-cyclopentene-1-carboxylate[8] according to Scheme I. The compound prepared in this manner had the same chemical–physical characteristics as **4b**.

Scheme I



Experimental Section

Melting points (uncorrected) were taken in capillary tubes on a Büchi apparatus. The ir and uv spectra were recorded with Perkin-Elmer 257 and Unicam SP 800 spectrophotometers, respectively. The nmr spectra were measured on a Jeol JMH-MH-60 spectrometer using TMS as internal standard.

Wittig Reaction of 4-Methyl-4-cyclopentene-1,3-dione with Triphenylcarbethoxymethylenephosphorane. A solution of 4-methyl-4-cyclopentene-1,3-dione[2] (2.2 g) in benzene (50 ml) was slowly added to triphenylcarbethoxymethylenephosphorane[3] (6.96 g, 2.0 mmol) and benzoic acid (0.25 g, 2.0 mmol) in benzene (50 ml). The resulting solution was refluxed for 2 hr; then petroleum ether (200 ml) was added and the mixture was cooled. After filtration of triphenylphosphine oxide, the solution was evaporated to yield an oil that was separated into three main fractions through chromatography using a silica gel column and ethyl acetate–cyclohexane (3:7) as the eluting solvent.

The first fraction was ethyl (*Z*)-3-methyl-4-oxo-2-cyclopenten-1-ylideneacetate (**1a**): tlc (silica gel) R_f 0.44; yield 0.4 g (11.1%); mp 50–51° from *n*-hexane; ir (Nujol) 1635 (C=C) and 1705 cm^{-1} (C=O); uv max (95% EtOH) 285.5 nm (ϵ 15,200); nmr (CCl_4) δ 1.20 (t, 3, $-CH_2CH_3$), 1.80 (s, 3, 3-CH_3), 2.75 (s, 2, 5-CH_2), 3.83 (q, 2, $-CH_2CH_3$), 5.20 (s, 1, =CHCOOEt), and 7.64 ppm (s, 1, 2-H).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.46; H, 6.58.

The second fraction was ethyl (*E*)-3-methyl-4-oxo-2-cyclopenten-1-ylideneacetate (**2a**): tlc (silica gel) R_f 0.38; yield 0.4 g (11.1%); mp 68–69° from *n*-hexane; ir (Nujol) 1635 (C=C) and 1700 cm^{-1} (C=O); uv max (95% EtOH) 282 nm (ϵ 20,100); nmr (CCl_4) δ 1.20 (t, 3, $-CH_2CH_3$), 1.80 (s, 3, 3-CH_3), 3.03 (d, $^4J \cong 1.5$ Hz,[7] 2, 5-CH_2), 3.83 (q, 2, $-CH_2CH_3$), 5.29 (s, 1, =CHCOOEt), and 6.73 ppm (s, 1, 2-H).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.54; H, 6.66.

The third fraction was ethyl 2-methyl-4-oxo-2-cyclopenten-1-ylideneacetate (**3a**): tlc (silica gel) R_f 0.26; yield 1.4 g (38.9%); bp 105–108° (8 mm) (with decomposition); ir (neat) 1643 (C=C) and 1705 cm^{-1} (C=O); uv max (95% EtOH) 276 nm (ϵ 9200); nmr (CCl_4) δ 1.22 (t, 3, $-CH_2CH_3$), 2.08 (s, 3, 2-CH_3), 3.01 (s, 2, 5-CH_2), 3.72 (q, 2, $-CH_2CH_3$), 5.42 (s, 1, =CHCOOEt), and 5.71 ppm (s, 1, 3-H).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.80; H, 6.86.

(*Z*)- and (*E*)-3-Methyl-4-oxo-2-cyclopenten-1-ylideneacetic Acid (1b and 2b). A suspension of **1a** (or **2a**) in 4 *N* HCl was refluxed for 30 min. The solution was then evaporated under reduced pressure and the resulting residue was crystallized from water.

Compound **1b** had mp 140–141°; ir (Nujol) 1645 (C=C), 1685, 1715 (C=O), and 2400–3500 cm^{-1} (OH).

Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.80; H, 5.51.

Compound **2b** had mp 196–198°; ir (Nujol) 1628 (C=C), 1675, 1715 (C=O), and 2300–3400 cm^{-1} (OH).

Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.85; H, 5.26.

2-Methyl-4-oxo-2-cyclopenten-1-ylideneacetic Acid (3b). This compound was prepared from **3a** using the procedure described for **1b**. It was crystallized from water: mp 178–180°; ir (Nujol) 1625 (C=C), 1670, 1690, 1720 (C=O), and 2300–3600 cm^{-1} (OH).

Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.95; H, 5.46.

Ethyl 3-Methyl-4-oxo-1-cyclopentaneacetate (4a). A. A solution of **1a** (or **2a**) in anhydrous ethanol was hydrogenated for 20 min over 10% palladium on charcoal at ambient pressure and temperature. The catalyst was filtered and washed with ethanol, and the filtrate was evaporated to yield an oil that was distilled under reduced pressure: bp 74–76° (5 mm); ir (neat) 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.10 (d, $^3J \cong 7.0$ Hz, 3, 3-CH_3), 1.27 (t, 3, $-CH_2CH_3$), 1.60–3.00 (m, 8, cyclopentane protons and $-CH_2COOEt$) and 4.16 ppm (q, 2, $-CH_2CH_3$).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.28; H, 8.81.

B. Esterification of the acid obtained from **6** with anhydrous ethanol and concentrated H_2SO_4 resulted in a product with the same physical characteristics as that obtained from method A.

Ethyl 2-Methyl-4-oxo-1-cyclopentaneacetate (5a). This compound was prepared from **3a** using the procedure described for **4a**. The resulting oil was distilled under reduced pressure: bp 68–72° (6 mm); ir (neat) 1735 cm^{-1} (C=O); nmr (CCl_4) δ 0.92 and 1.12 (2 d, $^3J \cong 6.5$ Hz, 3, 2-CH_3, trans and cis forms), 1.20 (t, 3, $-CH_2CH_3$), 1.50–3.00 (m, 8, cyclopentane protons and $-CH_2COOEt$), and 3.92 ppm (q, 2, $-CH_2CH_3$).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.25; H, 8.68.

3-Methyl-4-oxo-1-cyclopentaneacetic Acid (4b). A. Com-

pound **4a** was refluxed in 4 *N* HCl for 4 hr, and the solution was then evaporated and the resulting oil distilled under reduced pressure: bp 133–134° (0.25 mm); ir ($CHCl_3$) 1712, 1740 (C=O), and 2700–3600 cm^{-1} (OH); nmr ($CDCl_3$) δ 1.11 (d, $^3J \cong 7.0$ Hz, 3, 3-CH_3), 1.70–3.00 (m, 8, cyclopentane protons and $-CH_2COOH$), and 8.58 ppm (s, 1, –OH).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.45; H, 7.68.

B. A suspension of **6** (4.0 g) in 48% HBr (40 ml) was refluxed for 5 hr. Ammonium chloride was added and the solution was extracted with chloroform to yield 1.5 g of an oil with the same characteristics as that obtained with method A.

2-Methyl-4-oxo-1-cyclopentaneacetic Acid (5b). This compound was obtained from the corresponding ester **5a** using the procedure described for **4b**. The resulting oil was distilled under reduced pressure: bp 135–139° (0.3 mm); ir ($CHCl_3$) 1710, 1740 (C=O), and 2500–3600 cm^{-1} (OH); nmr ($CDCl_3$) δ 0.95 and 1.13 (2 d, $^3J \cong 6.5$ Hz, 3, 2-CH_3, trans and cis forms), 1.50–3.00 (m, 8, cyclopentane protons and $-CH_2COOH$), and 7.75 ppm (s, 1, –OH).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.62; H, 7.80.

Diethyl 3-Carbethoxy-3-methyl-4-oxo-1-cyclopentanemalonate (6). Diethyl malonate (6.4 g, 0.04 mol) and then ethyl 1-methyl-2-oxo-3-cyclopentene-1-carboxylate[8] (6.8 g, 0.04 mol) were added to a solution of Na (0.23 g, 0.01 mol) in anhydrous ethanol (12 ml) with cooling in a water bath. The reaction mixture was left for 2 hr at room temperature, and then decomposed with water and acidified with acetic acid. Extraction with ether and washing with saturated $NaHCO_3$ solution yielded an oil that was distilled under reduced pressure: bp 142–144° (0.04 mm); yield 9.7 g; ir (neat) 1730, 1740, and 1755 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{24}O_7$: C, 58.52; H, 7.37. Found: C, 58.61; H, 7.49.

Registry No.—**1a**, 51965-77-6; **1b**, 51965-78-7; **2a**, 51965-79-8; **2b**, 51965-80-1; **3a**, 51965-81-2; **3b**, 51965-82-3; **4a**, 51965-83-4; **4b**, 51965-84-5; *cis*-**5a**, 51965-85-6; *trans*-**5a**, 51965-86-7; *cis*-**5b**, 51965-87-8; *trans*-**5b**, 51965-88-9; **6**, 51965-89-0; 4-methyl-4-cyclopentene-1,3-dione, 30268-57-6; triphenylcarbethoxymethylenephosphorane, 1099-45-2; diethyl malonate, 105-53-3; ethyl 1-methyl-2-oxo-3-cyclopentene-1-carboxylate, 51965-90-3.

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Catalytic Reduction. III. Hydrogenation of Unsaturated Compounds over Borohydride Reduced Palladium[1,2]

Thomas W. Russell* and David M. Duncan

Department of Chemistry, Eastern New Mexico University, Portales, New Mexico 88130

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Partial reduction of multifunctional unsaturated compounds, using a variety of reagents or catalysts, is of considerable synthetic utility. In all preparatively useful conversions, it is of utmost importance that the reduction be highly selective as to site.

The product from the reaction between sodium borohydride and palladium(II) chloride catalyzes the partial hydrogenation of difunctional unsaturated compounds in a highly selective manner. A partial investigation reveals significant differences in the catalytic activities of this material from other palladium catalysts. In 1962, Polkovnikov, *et al.*,[3] reported that the rates of hydrogen uptake by a series of multifunctional olefins over borohydride reduced palladium were twice those over alkaline-formalin reduced palladium. Brown and Brown[4] in 1966 briefly described the activity of borohydride reduced palladium on some olefinic hydrocarbons.

Borohydride reduced palladium is a very versatile hydrogenation catalyst, as evidenced by the data in Table I. The material effectively and rapidly catalyzes the hydrogenation of carbon–carbon π bonds in a variety of solvents. Neither hydrogenation nor hydrogenolysis of nitrogen or oxygen functions σ bonded to carbon have been observed, with the exception of a slow ring opening of epoxides. Nitrogen–nitrogen and nitrogen–oxygen π bonds were reduced, whereas carbon–nitrogen and carbon–oxygen π bonds were not in the compounds studied. Presumably, the nitrogen–oxygen σ bond does undergo hydrogenolysis.

Experimental Section

Chemicals. All chemicals hydrogenated were reagent grade and were used directly from the bottles without further purification. Hydrogenation media were lower grade solvents. The palladium chloride was from Research Organic Chemicals. All organic chemicals, except the acids, amides, and azobenzene, were analyzed for purity by gas chromatography prior to use.

Catalyst Preparation. To a stirred solution of 0.443 g (2.5 mmol) of palladium chloride in 40 ml of absolute methanol, or other liquid at room temperature, was added 0.19 g (5.0 mmol) of powdered sodium borohydride over a 5–10-min period. Stirring was continued for 20 min, or until the evolution of a gas had ceased. The black reaction product settled rapidly when stirring was stopped.

The catalyst was used directly or stored under a liquid in a stoppered flask. The solvent was changed by decanting and washing twice.

Hydrogenation Procedure. To 2.5 mmol of catalyst and 40 ml of solvent in a Parr hydrogenation flask was added 100 mmol of the material to be hydrogenated. The flask was flushed with hydrogen, connected to a Parr low-pressure hydrogenator, and pressurized to 30 psi. Time and pressure were monitored. The conditions were maintained until no further uptake of hydrogen was observed. Reactions were begun at room temperature and conducted under ambient conditions.

The catalyst settled rapidly upon removing the reaction flask from the hydrogenator. The liquid was decanted for subsequent analysis. Following two washings, the catalyst was ready for reuse.

Product Analysis. All hydrogenation reaction mixtures were analyzed by gas chromatography. Only one product was detected in all cases. It was isolated and its infrared spectrum was taken on a Beckman IR-8. All spectra obtained were compared with those of authentic samples or those in the "Aldrich Library of Infrared Spectra."[5]

Results and Discussion

Applications. The versatility of borohydride reduced palladium as a hydrogenation catalyst can best be seen by a comparison of its activity with those of other catalysts.

No hydrogenolyses of nitrogen and oxygen groups σ bonded to carbon has been detected in alcohols, amides, amines, esters, ethers, or lactones studied. These results are in contrast with many findings that many palladium catalysts do effect hydrogenolysis of allylic and benzylic functions as well as reduction of a wide variety of other functions.[6]

Epoxides are very slowly opened, yielding monoalcohols at the sole products; however, since carbon–carbon π bonds are hydrogenated rapidly, the epoxide group should be unaffected in such a reaction over borohydride reduced palladium. It is of interest to note that the nickel analog did not open epoxides.[7]