by comparison with samples obtained by other routes[8,9] and confirmed by the ^1H NMR (300-MHz) spectrum.[9-11] ^1H NMR coupling constants J_{trans} and J_{cis} are listed in Table II and were derived either by direct means or from decoupling experiments.

Experimental Section

General Procedures. Analytical GLC was performed on a Perkin-Elmer 990 gas chromatograph equipped with a flame-ionization detector. The column used was a 55 m × 0.5 mm SP 2100 SCOT capillary, temperature programmed between 50 and 240 °C. ^1H NMR spectra were recorded in $CDCl_3$ on either a JEOL JNM-PMX 60 (60-MHz) or a Bruker CXP-300 (300-MHz) spectrometer. ^{13}C NMR spectra were determined on a Bruker WP-80 DS instrument. Mass spectra were determined on an AEI MS-3074 spectrometer at 70 eV in electron impact mode.

Starting Materials. *gem*-Dichlorocyclopropanes[13-16] were prepared by phase-transfer methods as previously described.[17,18] Ammonia was distilled from sodium prior to use. Me_2SO was distilled from calcium hydride and stored over molecular sieves under an atmosphere of nitrogen. Potassium *tert*-butoxide (Fluka) was used as received. Diphenylphosphine was prepared by the method of Gee et al.[19]

Typical Procedure. Diphenylphosphine (372 mg, 2.0 mmol) was added by syringe to a stirred solution of potassium *tert*-butoxide (224 mg, 2.0 mmol) in Me_2SO (10 mL) under N_2. After 10 min of stirring, 7,7-dichlorobicyclo[4.1.0]heptane (165 mg, 1.0 mmol) was added. The mixture was allowed to stir for 1 h and then was poured into water and extracted twice with petroleum spirit (bp 30-40 °C). The combined extracts were washed with water and dried. After the addition of an internal standard (2-chlorotoluene), the mixture was quantitatively examined by GLC. All yields were corrected for the detector responses.

Experiments in liquid ammonia were carried out at reflux on the same scale, except that the volume of liquid ammonia was 40 mL. After the reaction was complete, chilled (-40 °C) ether was added, and the reaction mixture was quenched by the cautious addition of ammonium nitrate (0.75 g). The ammonia was allowed to evaporate, and the mixture was diluted with water. The ether phase was washed with water, dried, and examined as before.

1,1-Bis(diphenylphosphinyl)-2-phenylcyclopropane. Dichloride **1g** (187 mg, 1.0 mmol) was added to a solution of potassium diphenylphosphide (2.0 mmol) in Me_2SO (10 mL) prepared as before. The mixture was stirred at room temperature for 1 h and then worked up as before and examined by GLC after the addition of an internal standard. The solvent was then removed, and 30% aqueous hydrogen peroxide (30 mL) was added cautiously in portions to a vigorously stirred solution of the residue in CH_2Cl_2 (30 mL). After 15 h of stirring, the organic phase was separated, washed with water, and dried. The crude product was subjected to flash chromatography on silica gel (25% ether/CH_2Cl_2) to afford the phosphine oxide **6g**: 210 mg; mp 210-211 °C; ^{13}C NMR δ 15.2 (t), 26.6 (t, J_{P-C} 78 Hz), 29.1 (d), 125-133 (unresolved); ^1H NMR (60 MHz) δ 1.7-3.2 (m, 3 H), 6.6-8.1 (m, 25 H); MS, *m/z* (relative intensity) 518 (M^+, 100), 412 (28), 288 (8), 201 (12); exact mass *m/z* 518.1564, calcd for $C_{33}H_{28}O_2P_2$ *m/z* 518.1565.

Preparative Experiments. The following example is illustrative. Diphenylphosphine (5.58 g, 30 mmol) was added dropwise to a stirred solution of potassium *tert*-butoxide (3.37 g, 30 mmol) in Me_2SO (50 mL) under N_2. The flask was immersed in a bath of cold water during both the addition and the subsequent steps. After 15 min of stirring, 7,7-dichlorobicyclo[4.1.0]heptane (3.30 g, 20 mmol) was added dropwise, and the mixture was allowed to stir for 1 h. After this time, it was poured into water (100 mL) and extracted with pentane (2 × 25 mL). The combined extracts were washed several times with water. The dried extracts were concentrated through a Vigreux column (15 cm), and the residue was distilled with a short-path apparatus to afford a mixture of **2a** and **3a**: 1.98 g, 76%; bp 60-61 °C (10 mmHg) [lit.[8] bp 78 °C (16 mmHg)].

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Registry No. **1a**, 823-69-8; **1b**, 6498-44-8; **1c**, 3722-08-5; **1d**, 5685-42-7; **1e**, 20202-10-2; **1f**, 3141-45-5; **1g**, 2415-80-7; **2a**, 18688-22-7; **2b**, 24266-06-6; **2c**, 109125-04-4; **2d**, 64139-65-7; **2e**, 35731-78-3; **2f**, 14123-41-2; **2g**, 17651-00-2; **3a**, 18688-21-6; **3b**, 24266-07-7; **3c**, 109125-05-5; **3d**, 64139-64-6; **3e**, 35731-79-4; **3g**, 17650-99-6; **6g**, 109125-06-6; potassium diphenylphosphide, 15475-27-1.

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Exceptionally Slow Reduction of Phenylmalonic Acid by Borane-THF via Cyclic (Phenylmalonoxy)borane

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The remarkable ease with which carboxylic acids, both aliphatic and aromatic, are reduced by borane-tetrahydrofuran (BH_3·THF) has been previously described.[1,2]

$$RCOOH \xrightarrow{BH_3\cdot THF} \underset{>95\%}{RCH_2OH}$$

R = alkyl or aryl

Brown and co-workers have recently established the details of the borane reduction mechanism which must proceed through the intermediate formation of monoacyloxyborane, either formed directly from the carboxylic acid and borane or formed by a redistribution reaction of diacyloxyborane with borane.[3]

During synthesis of the labeled new anticonvulsant [^{14}C]felbamate, we have observed that the reduction of phenylmalonic acid (**1**) even with an excess of borane-tetrahydrofuran is unusually slow. This reaction proceeded sluggishly at 0 °C, requiring 16 h to yield only 35% of 2-phenyl-1,3-propanediol and unreacted starting material.[4] Moreover, the yield was not enhanced by the use of bo-

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Table I. Reduction of Carboxylic Acids with Borane–THF in Tetrahydrofuran at 0 °C[a]

carboxylic acid	time, h	H_2 evolvd, mmol/mmol of FG	total H^- consumd, mmol/mmol of FG	H^- used for reductn, mmol/mmol of FG
benzoic	0.25	1.00	1.08	0.08
	1.0	1.00	1.98	0.98
	3.0	1.00	2.46	1.46
	12.0	1.00	2.95	1.95
	24.0	1.00	3.00	2.00
phenylacetic	0.25	1.09	3.09	2.00
	0.5	1.09	3.09	2.00
	1.0	1.09	3.09	2.00
phenylmalonic	0.25	1.44	1.95	0.51
	0.5	1.50	2.05	0.56
	1.0	1.50	2.06	0.56
	4.0	1.50	2.17	0.67
	24.0	1.50	2.31	0.81
(phenylmalonoxy)borane[b]	0.25	0.39	0.87	0.48
	0.5	0.46	0.97	0.52
	1.0	0.49	1.02	0.53
	4.0	0.49	1.19	0.70
	24.0	0.49	1.24	0.74
phenylmalonic[c]	0.25	1.41		
	0.5	1.49	1.86	0.37
	1.0	1.49	1.95	0.46
phenylmalonic[d]	0.10	0.95	1.70	0.75
	0.25	1.08	1.84	0.76
	0.5	1.14	1.90	0.76
	1.0	1.18	2.08	0.90
	4.0	1.19	2.23	1.04
	24.0	1.19	2.37	1.18

[a] 0.25 M in functional group (FG) in substrate and 1.0 M in hydride in BH_3–THF unless otherwise indicated. [b] 0.25 M in FG in substrate and 0.65 M in hydride in BH_3·THF. [c] 0.25 M in FG in substrate and 0.75 M in hydride in BH_3·THF. [d] At −20 °C.

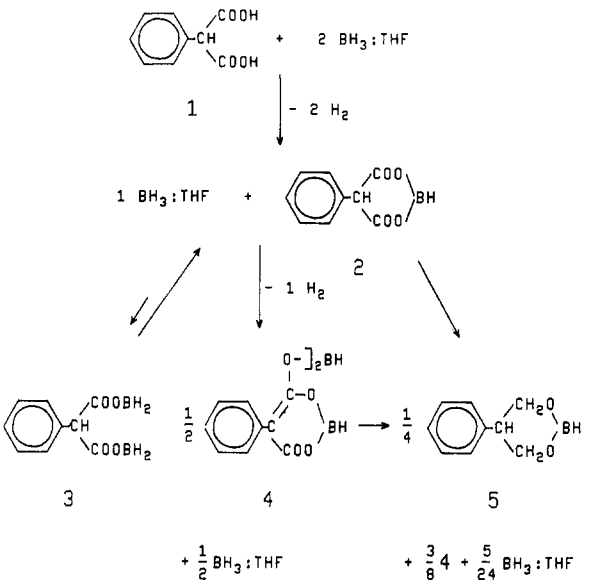
rane–dimethyl sulfide,[5] which led to only 23% of the product. Therefore, we undertook a study of the reaction of phenylmalonic acid with borane–THF under mild, controlled reaction conditions.

The general procedure adopted is to add 12 mmol of H^- in borane–THF solution to 3.0 mmol of the carboxylic group in the compound in sufficient THF unless otherwise indicated. This makes the reaction mixture 0.33 M in BH_3 and 0.25 M in the functional group (FG) in substrate. The reactions are carried out at a constant temperature (0 °C). Aliquots are removed at appropriate intervals of time and analyzed for residual hydride by hydrolysis. The three representative carboxylic acids studied are benzoic acid, phenylacetic acid, and phenylmalonic acid.

With benzoic acid, the most inert among the acids, addition of a solution of borane–THF in THF resulted in the evolution of 1 equiv of hydrogen in 0.25 h and led to complete reduction in 24 h. The corresponding reaction of phenylacetic acid containing an acidic α-hydrogen was completed in 0.25 h, at which time 1.09 equiv of hydrogen was released (Table I). In the case of phenylacetic acid the data indicate that the reduction successfully competes with active α-hydrogen abstraction for the borane intermediate. The reaction of **1**, however, was confirmed to be quite slow. It essentially stopped in 4 h showing only a 33% uptake of hydride. The hydrogen evolution was 2.8 equiv in 0.25 h and 3 equiv in 0.5 h.

It has been previously reported that the reaction of benzoic acid with borane–THF stops at the bis(benzoyloxy)borane stage.[6] Addition of borane–THF to **1** in a 1:1 molar ratio resulted in the evolution of only 2 equiv of hydrogen and the expected formation of a cyclic (phenylmalonoxy)borane (**2**) as indicated in Scheme I. The FT-IR spectrum of **2** in THF showed a strong absorption band at approximately 1600 cm^{-1}, indicating that the carbonyl group is coordinated to boron (⟩C=O → B⟨).[3] Moreover, a strong peak at approximately 1560 cm^{-1} was missing, indicating the absence of the B–H bridge while a band at 2470 cm^{-1} was indicating the existence of monomeric ⟩BH.[3] The ^1H FT-NMR spectrum of **2**·THF in chloroform-*d* showed resonances at 7.36 (singlet) and 4.61 (singlet) ppm, corresponding to the aromatic and benzylic protons, respectively. The ^{11}B FT-NMR spectrum of **2** in THF showed resonance at +2.98 ppm (relative to BF_3·OEt_2), as compared to +4.8 and +3.0 ppm of bis(benzoyloxy)borane–THF and bis(chloroacetoxy)borane–THF complex, respectively.[3] Although a THF solution of **2** was evaporated to dryness at room temperature, a plateau in the time vs. sample weight curve showed the existence of only pure **2** (mp 159–161 °C) without any solvent addition compound. A solution of **2** in THF is reasonably stable at 0 °C but appears to deteriorate slowly over 2 weeks. However, this compound is remarkably stable when stored in the solid state even at room temperature.

Scheme I



Reduction of the intermediate **2** with 5 H^- equiv in BH_3·THF or of the acid **1** with 8 H^- equiv proceeded at 0 °C with approximately the same rate (Table I). After 24 h, analysis of the precipitated reaction aliquots in THF by ^{11}B NMR revealed two major resonances at −0.9 and +25.9 ppm, corresponding to the unreacted BH_3·THF and the reduced product **5**, respectively.[7] Apparently the reduction proceeded through the intermediate **2** without an exchange with free BH_3·THF to form **3** (Scheme I), which would be rapidly reduced as shown in Table I by the reduction of phenylacetic acid with borane–THF. Treatment of **2** with $^1/_3$ BH_3·THF resulted in the evolution of 0.52 equiv of hydrogen and only 5% reduction in 2 h (by analysis of residual hydride by hydrolysis). The ^{11}B NMR spectrum of the reaction mixture showed three compounds: unreacted starting material **2** (+2.9 ppm), **3** (+25.7 ppm) as a reduction product, and **4** (+2.9 and +19.8

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ppm) as the second intermediate. Furthermore, by treatment of 1 with borane–THF in a 1:2 ratio, 3 equiv of hydrogen was evolved, and only 19% of hydride uptake in 0.5 h and 23% of reduction in 1 h were achieved (Table I and Scheme I). The ^{11}B NMR of the partially precipitated reaction aliquot showed two compounds corresponding to 3 (+26.1 ppm) and 4 (+2.9 and +19.2 ppm).[8] These experiments clearly indicate that at 0 °C the α-hydrogen abstraction is more predominant than the reduction. The reduction proceeding through the intermediate 4 is exceptionally slow and essentially stops the reaction.

Consequently, to control the α-hydrogen abstraction from 1 by borane–THF, the reaction was carried out at a lower temperature. Addition of BH_3·THF to 1 in a ratio of 8:3 at −20 °C resulted in the evolution of 2 equiv of hydrogen and consumption of 37% active hydride for reduction in 5 min. It appeared that the course of the reaction at −20 °C was significantly faster in the first 5 min than at 0 °C. This indicates to us that the reduction via 2 is probably much faster than through the intermediate 4 formed by α-hydrogen abstraction from 2.

In conclusion, an important new intermediate formed by reduction of 1 with borane–THF was identified as the relatively stable cyclic 2. From this intermediate a second (4) is formed by α-hydrogen abstraction. This can be suppressed by lowering the temperature to −20 °C. Intermediate 4 appears to be more resistant to further reduction than 2.

Experimental Section

^{11}B FT-NMR and ^{1}H FT-NMR spectra were recorded on a Jeol FX-90Q FT-NMR spectrometer. All ^{1}H chemical shifts are relative to tetramethylsilane (δ 0), and ^{11}B chemical shifts are relative to boron trifluoride etherate (δ 0). FT-IR spectra were recorded on FX-6160 FT-IR spectrometer. All glassware was dried thoroughly in a drying oven and cooled under a dry stream of nitrogen. All reduction experiments were carried out under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer the solution. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Tetrahydrofuran (THF) was dried with excess lithium aluminum hydride, distilled under nitrogen immediately prior to use. Borane–THF was the commercial product and standardized by hydrolyzing a 1 mL aliquot of the solution with glycerine–water–THF mixture and measuring the hydrogen evolved. Carboxylic acids were the commercial product of the highest purity.

Procedure for the Rate Study. The reduction of phenylmalonic acid is representative. Two 50-mL round-bottom flasks with side arm were dried in an oven and cooled down in a dry nitrogen atmosphere. The first flask was equipped with a rubber syringe cap, a magnetic stirring bar, and a reflux condenser, connected to a gas buret. Then 3 mL (1.5 mmol) of a 0.5 M solution of phenylmalonic acid was injected into the reaction flask, followed by 4.5 mL of dry THF (the resulting solution contained 1.0 M in hydride and 0.25 M in functional group). The flask was immersed in an ice bath and cooled to 0 °C. Then 4.52 mL (12 mmol of hydride) of 0.89 M borane solution in THF was added slowly. There was evolved 110 mL (4.33 mmol, 1.44 mmol/FG) of hydrogen in 0.25 h. The rate of hydrogen evolved was followed with time. The results are summarized in Table I.

The second reaction flask was prepared in the same manner. Aliquots (2.0 mL) were withdrawn at various time intervals and analyzed by hydrolysis. A blank experiment was performed in which THF was substituted for the acid. From the difference, the number of millimoles of hydride used for reduction per millimole of acid and hence the percentage of reaction was calculated. The results are given in Table I. The isolation of the diol was described in a previous study.[4]

(Phenylmalonoxy)borane. The apparatus is the same as that described previously. In a 50-mL, round-bottom flask was placed 3 mL (1.5 mmol) of 0.5 M solution of phenylmalonic acid followed by 4.5 mL of dry THF. The mixture was cooled to 0 °C, and then 1.3 mL of 0.89 M BH_3·THF (1.5 mmol) was slowly added. Hydrogen evolution (72 mL, 2.84 mmol) was over in 1.5 h. The glass apparatus was weighed. A small piece of vacuum tubing was attached to the connecting tube. It was then immersed in a water bath at room temperature and connected to a vaccum setup. The flask was then opened slowly to the vaccum, and the weight change was noted with time. A white, crystalline solid whose weight corresponds to $PhCH(CO_2)_2BH$, 0.28 g (98%), mp 159–161 °C: IR (THF) 2470 (br s), 1725 (sh), 1702 (s), 1600 (s), 1560 (w), 1502 (s), 1330 (m), 1290 (vs), 1090 (m), 990 (m), 770 (m), 690 (m) cm $^{-1}$; ^{1}H NMR ($CDCl_3$) δ 4.61 (s, 1 H, benzylic) and 7.36 (s, 5 H, Ar); ^{11}B NMR (THF) +2.98 ppm.

Registry No. 1, 2613-89-0; 2, 109306-89-0; 3, 109306-90-3; 4, 109306-91-4; 5, 109306-92-5; benzoic acid, 65-85-0; phenylacetic acid, 103-82-2.

(8) It appears that the second intermediate, 4, slowly precipitates out of the solution during the course of the reaction, as indicated by the decrease in the ^{11}B NMR resonances of 4 and the increase in the amount of precipitate present.

Hypervalent Iodine Oxidation of *p*-Alkoxyphenols and Related Compounds: A General Route to *p*-Benzoquinone Monoacetals and Spiro Lactones

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Quinone monoacetals are potentially attractive compounds as regiospecific quinone equivalents in organic synthesis and the chemistry of the acetals is summarized in recent reviews.[1] They serve as precursors to various types of natural products such as tropolones,[2] ryanodol,[3] α-tocopherol,[4] and anthracyclines.[5] These quinones are generally prepared by (i) chemical oxidation of 4-alkoxy- or 4-(aryloxy)phenols with oxidizing reagents such as copper(II) species,[6] ceric salts,[7] and thallium(III) nitrate (TTN),[8] (ii) electrochemical oxidation of *p*-methoxyphenols[9] or their trimethylsilyl ethers,[10] and (iii) monohydrolysis of quinone bisacetals.[1b,11] Althouth the first method (i) is the most facile and shortest route to quinone monoacetals of these methods, it often employs highly

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