extensively used for the oxidation of substituted hydrazones and aroylhydrazones.[11-13] The oxidation of bis(aroylhydrazones) Ib, Ie, Ik, Iq, and Ir with lead tetraacetate was carried out by a gentle heating for 2–3 hr. The yields of corresponding isoimides were almost twice those obtained by Stollé's method.[8]

Experimental Section

Melting points are uncorrected and were determined with a Kofler hot-stage apparatus. Ir spectra were measured as Nujol mulls with a Beckman IR-4 or Perkin-Elmer 257 spectrophotometer. Nmr spectra were obtained in $CDCl_3$ with a Varian A-60A spectrometer.

Preparation of Bis(aroylhydrazones) of α Dicarbonyl Compounds.—Those of biacetyl were prepared[14] by heating in ethanol or *n*-propyl alcohol 1 mol of biacetyl with 2.2 mol of the corresponding aroylhydrazines for 6 hr.

The bis(aroylhydrazones) of other α diketones were prepared[15,16] by heating in a sealed tube 1 mol of diketone with 2.2 mol of aroylhydrazines for 12 hr at ~150°. The yields in both methods were 70–90%. The analytical data of the prepared compounds were in agreement with their structure and/or their melting points were in agreement with those of the literature.

Oxidation of Bis(aroylhydrazones) of α-Dicarbonyl Compounds. A. With Mercuric Oxide and Iodine.[8]—A mixture of 0.01 mol of bis(benzoylhydrazone), 0.025 mol of mercuric oxide, 0.025 mol of iodine, and 0.5 g of magnesium oxide in 80 ml of dry ether was heated under stirring for 15 hr. After filtration of the mixture the ethereal solution was washed with potassium iodide solution, then with sodium thiosulfate and water, and finally dried with anhydrous sodium sulfate. The oxidation products were obtained after evaporation and crystallization. The aroylaminotriazoles were separated by fractional crystallization or by chromatographic analysis on aluminum oxide. (For the analytical data of the prepared compound see Table I.) The nonoxidized starting material was recovered by treating the precipitate containing the inorganic material with dilute hydrochloric acid and recrystallization.

B. Oxidation with Lead Tetraacetate.—To a mixture of 0.002 mol of bis(aroylhydrazone) in 20 ml of methylene chloride, a solution of 0.004 mol of lead tetraacetate in 20 ml of methylene chloride was added and the mixture was gently heated for 2–3 hr, or it was left at room temperature for 10 hr. The methylene chloride solution was treated with water, and filtered and the organic layer was washed with sodium bisulfite solution, sodium carbonate solution, and water and then dried. The isoimides were obtained after evaporation and recrystallization. They were identical with those obtained by method A.

Registry No.—Ia, 34502-22-2; Ib, 34502-23-3; Ic, 34502-24-4; Id, 34502-25-5; Ie, 34502-26-6; If, 34502-27-7; Ig, 34502-28-8; Ih, 34502-29-9; Ii, 34502-30-2; Ij, 34502-31-3; Ik, 34502-32-4; Il, 34502-33-5; Im, 34502-34-6; In, 34502-35-7; Io, 34502-36-8; Ip, 34502-37-9; Iq, 34502-38-0; Ir, 34502-39-1; IIa, 34566-67-1; IIb, 19226-34-7; IIc, 34502-40-4; IId, 34502-41-5; IIe, 34502-42-6; IIf, 34502-43-7; IIg, 34502-44-8; IIh, 34502-45-9; IIi, 34502-46-0; IIj, 34519-95-4; IIk, 34502-47-1; III, 34519-96-5; IIm, 34502-48-2; IIn, 34502-49-3; IIp, 34599-20-7; IIq, 34502-50-6; IIr, 34519-97-6; IIIm, 34502-51-7; IIIn, 34502-52-8; IIIo, 34502-53-9.

Acknowledgment.—The authors are indebted to the National Hellenic Research Foundation for financial support.

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An Asymmetric Synthesis of Alcohols, Amines, and Amino Acids

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Received December 7, 1971

Asymmetric reduction of the ketone moiety has been the subject of much recent investigation.[2] We have reported previously the reduction and reductive amination of aldehydes and ketones using sodium cyanoborohydride ($NaBH_3CN$) as a reducing agent.[3] This new method proved to be especially suitable for the synthesis of isotopically labeled amino acids from the corresponding substituted pyruvic acids. In the hope that we might extend this method to allow preparation of optically active amino acids, we have investigated the use of the structurally similar (*e.g.*, H_3B–X, where X is an electron-withdrawing group) amine–boranes as reducing agents. We were encouraged by a previous report of aldehyde and ketone reduction by the amine–borane system;[4] during the course of our work a detailed study of this reduction appeared.[5] In this report we confirm that both reduction and reductive amination of ketones can be carried out with asymmetric induction to give optically active products, although the optical purities obtained in this synthesis are quite low.

We chose for this study (*R*)(+)- and (*S*)(−)-α-phenethylamine–boranes **2**, which were prepared in 80% yield from the corresponding amine hydrochlorides **1**.[6] The method was initially tested by examining the reduction of acetophenone[7] and 2-heptanone with 1 molar equiv (3 hydride equiv) of amine–borane; the results are summarized in Table I. To ascertain that the rotations were not arising from a trace of α-phenethylamine remaining in the alcohols after work-up, a control experiment was carried out in which alcohol of known optical purity was mixed with (*S*)(−)-α-phenethylamine and subjected to the reaction work-up. The isolated alcohol was free of amine by glpc analysis, and the rotation of the isolated alcohol was identical with that of the starting alcohol. It is apparent that asymmetric reduction did occur, although the optical purities were disappointingly low, presumably owing to the large distance between the asymmetric carbon of the reducing agent and the developing tetrahedral carbon of the product in the transition state. A

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(7) During the course of this study the reduction of acetophenone by (*S*)-amphetamine–borane was reported: J. C. Fiand and H. B. Kagan, *Bull. Soc. Chim. Fr.*, 2742 (1969). Low optical yields were obtained, and the absolute configuration of the product was ambiguous, erroneously reported as (*S*)(+)-phenethanol.

TABLE I

REDUCTION OF 2-HEPTANONE AND ACETOPHENONE WITH (*R*)(+)- OR (*S*)(−)-α-PHENETHYLAMINE–BORANES

Ketone	Confign of 2	Solvent (temp, °C)	Product	Product confign	Product $[\alpha]^{25}D$, degree (*c*, g/100 ml)	Yield, %[a]	Optical purity, %
Acetophenone	*R*(+)	Benzene (reflux)	α-Phenethanol	*R*(+)	+1.80 ± 0.07[b] (6.57)	73	3.3 ± 0.2
Acetophenone	*S*(−)	Benzene (reflux)	α-Phenethanol	*S*(−)	−1.55 ± 0.09[b] (7.23)	66	2.8 ± 0.3
Acetophenone	*R*(+)	CCl_4 (reflux)	α-Phenethanol	*R*(+)	+1.35 ± 0.07[b] (7.49)	76	2.5 ± 0.2
Acetophenone	*R*(+)	Methanol (reflux)	α-Phenethanol	*S*(−)	−0.81 ± 0.07[b] (7.06)	54	1.5 ± 0.1
Acetophenone	*R*(+)	Methanol (25)	α-Phenethanol	*S*(−)	−1.20 ± 0.20[b] (2.74)	58	2.2 ± 0.4
Acetophenone	*S*(−)	Methanol (25)	α-Phenethanol	*R*(+)	+1.04 ± 0.08[b] (7.32)	51	1.8 ± 0.4
2-Heptanone	*R*(+)	Methanol (25)	2-Heptanol	*S*(+)	+0.31 ± 0.04[c] (7.25)	58	2.7 ± 0.4
2-Heptanone	*S*(−)	Methanol (25)	2-Heptanol	*R*(−)	−0.26 ± 0.03[c] (7.05)	51	2.3 ± 0.3
2-Heptanone	*S*(−)[d]	Methanol (25)	2-Heptanol	*R*(−)	−0.23 ± 0.07[c] (2.66)	37	2.2 ± 0.5
2-Heptanone	*S*(−)	Benzene (reflux)	2-Heptanol	*R*(−)	−0.35 ± 0.03[c] (7.36)	76	3.1 ± 0.4
2-Heptanone	*S*(−)	CCl_4 (reflux)	2-Heptanol	*R*(−)	−0.19 ± 0.02[c] (11.40)	91	1.7 ± 0.2

[a] Yields were determined by glpc analysis. [b] Rotations were measured in diethyl ether. [c] Rotations were measured in 95% ethanol. [d] One hydride equivalent of amine–borane **2** was used.

TABLE II

REDUCTION AMINATION OF KETONES WITH (*R*)(+)- AND (*S*)(−)-α-PHENETHYLAMINE–BORANES AND AMMONIA IN METHANOL AT 25°

Ketone	Confign of 2	Product	Product confign	Product $[\alpha]^{25}D$, degree (*c*, g/100 ml)	Yield, %[a]	Optical purity, %
2-Octanone[a]	*R*(+)	2-Octylamine	*S*(+)	+0.45 ± 0.09[b] (2.20)	28	1.6 ± 0.3
2-Octanone[a]	*S*(−)	2-Octylamine	*R*(−)	−0.27 ± 0.09[b] (2.23)	33	1.1 ± 0.3
Pyruvic acid[c]	*S*(−)	Alanine	*S*(+)	+0.32 ± 0.11[d] (3.35)	71	2.2 ± 0.5
2-Ketoglutaric acid[c]	*S*(−)	Glutamic Acid	*R*(−)	−0.97 ± 0.09[d] (3.60)	72	3.1 ± 0.3
Phenylpyruvic acid[c]	*S*(−)	Phenylalanine	*R*(+)	+1.37 ± 0.25[e] (0.81)	66	4.0 ± 0.7
Phenylpyruvic acid[f]	*S*(−)	Phenylalanine-^{15}N[g]	*R*(+)	+1.38 ± 0.35[e] (0.87)	25	4.0 ± 1.0

[a] A 10-fold excess of ammonia was used. [b] The rotation was measured on the benzamide in ethanol. [c] A 5-fold excess of ammonia was used. [d] Rotation was measured in 5 *N* HCl. [e] Rotation was measured in H_2O. [f] 1.2 equiv of $^{15}NH_3$ were used. [g] Isotopic analysis of the product showed >88% ^{15}N.

surprising result was the solvent effect on the product configuration in the case of acetophenone. While the reduction of 2-heptanone afforded a product having an absolute configuration opposite to that of the amine–borane used in all solvents investigated (*i.e.*, *R* amine–borane → *S* alcohol), this observation held only for the reduction of acetophenone in methanol. Reduction of acetophenone in benzene or carbon tetrachloride, however, gave a product with absolute configuration opposite to that obtained in methanol. Unfortunately, the low optical purities (and hence the small transition-state energy differences) observed in these reductions would seem to preclude any meaningful discussion of transition-state complex geometry. It is apparent, however, that these small energy differences are affected by changes in solvation of the complex.

Asymmetric reductive aminations were carried out according to the procedure described earlier,[3] using amine–borane **2** in place of $NaBH_3CN$; the results are summarized in Table II. Yields of amine obtained from 2-octanone are low, owing to the fact that the acid-independent amine–borane reduction[5] of ketone to alcohol is competing effectively with the reductive amination. This was verified by the fact that 2-octanol could be isolated in 30–50% yield from these reductive aminations. Finally, it is interesting to note that the use of amine–boranes in the synthesis of amino acids gives yields appreciably higher than were obtained using sodium cyanoborohydride.[3]

$$\underset{\mathbf{1a,b}}{PhCH(CH_3)NH_2\cdot HCl} \xrightarrow[DME]{NaBH_4} \underset{\mathbf{2a,b}}{PhCH(CH_3)NH_2\text{–}BH_3}$$

a = *R*(+)
b = *S*(−)

$$RCOCH_3 + 2 \longrightarrow R\overset{*}{C}H(OH)CH_3 \text{ (1–3\% optical purity)}$$

$$RCOR' + NH_3 + 2 \longrightarrow R\overset{*}{C}H(R')NH_2 \text{ (1–4\% optical purity)}$$

Experimental Section[8]

(*R*)(+)- and (*S*)(−)-α-Phenethylamine–boranes (2a and 2b).—To a flame-dried 1-l. flask fitted with a dropping funnel, a nitrogen inlet, and a magnetic stirrer was added 28.3 g (0.18 mol) of (*S*)(−)-α-phenethylamine hydrochloride.[9] The salt was covered with dry dimethoxyethane (distilled from $LiAlH_4$) and cooled in an ice bath, and a solution of sodium borohydride (11.0 g, 0.29 mol) in 500 ml of dimethoxyethane was slowly added over 1.5 hr to the stirred suspension (*CAUTION:* hydrogen evolution occurs throughout the addition). After stirring at 0° for an additional 1.5 hr, the suspension was filtered and the filtrate was evaporated *in vacuo* to give a white semisolid residue. Petroleum ether (100 ml) was added, and the crystalline amine–borane **2b** was collected by filtration (yield 26.8 g). Recrystallization from methylene chloride–petroleum ether afforded

(8) Melting points were obtained in capillary tubes and are uncorrected. Analytical and preparative gas chromatograms were obtained on a Varian Aerograph 90-P3 instrument using 0.25 in. × 10 ft columns. All identifications by glpc analysis were made by peak enhancement with authentic samples. Optical rotations were obtained on a Perkin-Elmer Model 141 polarimeter in a 1-dm cell; concentrations *c* are expressed in g/100 ml. Elemental analyses were performed by the Microanalytical Laboratory, University of Minnesota. Anhydrous magnesium sulfate was used as drying agent throughout.

(9) Available in 97.5% optical purity from Aldrich Chemical Co.

(bp 30–60°) 19.8 g (82%) of **2b**: mp 119–120°; $[\alpha]^{25}D$ −77.2° (*c* 1.84, benzene); 97.5% optically pure.

Anal. Calcd for $C_8H_{14}BN$: C, 71.13; H, 10.47; N, 10.39. Found: C, 71.09; H, 10.29; N, 10.35.

(*R*)(+)-α-Phenethylamine–borane (**2a**) was prepared in 78% yield as described above: mp 119–120°; $[\alpha]^{25}D$ +77.3° (*c* 2.12, benzene).

Reduction of Ketones with 2a and 2b. General Procedure.—To a solution of the ketone (4 mmol) in 20–25 ml of the appropriate solvent was added 4 mmol of **2a** or **2b** (97.5% optically pure), and the resulting solution was stirred for 4 hr at the specified temperature. The solvent was removed *in vacuo*, and the residue was stirred with excess 6 *N* HCl until no further hydrogen evolution (from hydrolysis of unreacted amine–borane) was observed. The aqueous solution was saturated with sodium chloride and extracted with 3 20-ml portions of ether. The combined extracts were washed with 10-ml portions of 3 *N* HCl, 6 *N* NaOH, and brine, and the ether solution was then dried and evaporated *in vacuo*. The colorless residual oil was analyzed by glpc (15% FFAP on Chromosorb W and 15% Carbowax 20M on Chromosorb W). A sample was purified by preparative glpc, and the optical rotation was measured on this purified sample as a solution in ether (α-phenethanol) or 95% ethanol (2-heptanol). Absolute configuration and optical purity were determined from the known values of $[\alpha]^{25}D$ +54.86° (ether) for (*R*)(+)-α-phenethanol[10] and $[\alpha]^{25}D$ −11.4° (EtOH) for 2-heptanol.[11]

Reductive Amination of 2-Octanone with 2a or 2b and Ammonia.—A solution of 2-octanone (2.24 g, 17.5 mmol) was dissolved in 50 ml of methanol containing ammonia (3.2 ml of liquid NH_3, 140 mmol) and ammonium bromide (3.43 g, 35 mmol), and either **2a** or **2b** (2.36 g, 17.5 mmol) was added. The resulting solution was stirred at 25° for 48 hr. The methanol was removed *in vacuo*, and the residue was stirred for 10 min with excess 6 *N* HCl. The aqueous solution was washed with two 10-ml portions of ether (2-octanol could be isolated from this ether extract if desired). Solid potassium hydroxide was added to the aqueous layer until the pH of the solution was >12, and the amines were extracted with three 25-ml portions of ether. The combined extracts were dried and evaporated *in vacuo* to give a mixture of α-phenethylamine and 2-octylamine. A sample of 2-octylamine was isolated by preparative glpc (15% FFAP on Chromosorb W) and was converted to its benzamide, mp 78–79.5° (86% yield). Absolute configuration and optical purity were determined by comparison of the rotation of the benzamide with the literature value[12] for (*R*)(−)-2-octylamine benzamide of $[\alpha]^{25}D$ −28.5° (EtOH).

Reduction Amination of α-Keto Acids with 2a or 2b and Ammonia. General Procedure.—To a solution of 0.9 ml (40 mmol) of liquid ammonia and 0.98 g (10 mmol) of ammonium bromide in 30 ml of methanol was added 5 mmol of α-keto acid or α-keto acid sodium salt. The resulting solution was stirred for 1 hr at 25°. (*S*)(−)-α-Phenethylamine–borane (0.68 g, 5 mmol) was added, and the solution was stirred at 25° for 36–72 hr. Methanol and excess ammonia were removed *in vacuo*, and the residue was brought to pH 1 with 12 *N* HCl. After stirring for 15 min, the acidic solution was made basic with excess ammonium hydroxide and washed with two 15-ml portions of ether (ether wash discarded). The aqueous solution was evaporated *in vacuo*. The residue was dissolved in a minimum volume of distilled water and added to the top of a Dowex 50 column (acid form, 250-mequiv capacity). The column was washed with 1 l. of distilled water, and the amino acid was then eluted with 250 ml of 2 *N* ammonium hydroxide. The ammonium hydroxide solution was evaporated *in vacuo* to give the amino acid as a colorless solid. Tlc analysis on cellulose and silica gel plates (butanol–acetic acid–water, 4:1:1) showed one spot identical with that of an authentic sample (detected by ninhydrin staining). Absolute configuration and optical purity were determined by comparison of the rotation of the amino acids with the published values: (*S*)(+)-alanine, observed $[\alpha]^{25}D$ +0.32 ± 0.11° (*c* 1.85, 5 *N* HCl), lit.[13] $[\alpha]^{25}D$ +14.6° (5 *N* HCl); (*R*)(−)-glutamic acid, observed $[\alpha]^{52}D$ −0.97 ± 0.09° (*c* 3.60, 5 *N* HCl), lit.[14] $[\alpha]^{25}D$ −31.8° (5 *N* HCl); (*R*)(+)-phenylalanine, observed $[\alpha]^{25}D$ +1.37 ± 0.25° (*c* 0.81, H_2O), lit.[15] $[\alpha]^{25}D$ +34.5° (H_2O).

Phenylalanine-^{15}N.—Sodium phenylpyruvate (0.47 g, 2.5 mmol), ammonium nitrate-^{15}N (0.40 g, 5.0 mmol, 95% $^{15}NH_4NO_3$), and **2b** (0.68 g, 5 mmol) were allowed to react for 36 hr and worked up as described above to give 105 mg (25%) of phenylalanine, $[\alpha]^{25}D$ +1.38 ± 0.35° (*c* 0.87, H_2O). A sample was purified by preparative tlc (silica gel G, 4:1:1 butanol–acetic acid–water) for nitrogen isotope mass spectral analysis, minimum ^{15}N composition 88%.[16]

Registry No.—**2a**, 34566-00-2; **2b**, 34566-01-3; 2-heptanone, 110-43-0; acetophenone, 98-86-2; (*R*)-(+)-α-phenethanol, 1517-69-7; (*S*)(−)-α-phenethanol, 1445-91-6; (*S*)(+)-2-heptanol, 6033-23-4; (*R*)(−)-2-heptanol, 6033-24-5; (*S*)(+)-2-octylamine, 34566-04-6; (*R*)(−)-2-octylamine, 34566-05-7; (*S*)(+)-alanine, 3081-24-1; (*R*)(−)-glutamic acid, 6893-26-1; (*R*)(+)-phenylalanine, 673-06-3; (*R*)(+)-phenylalanine-^{15}N, 673-06-3.

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Pyrolysis of 2-Acetoxy-2-methylcyclopentane-1,3-dione and 3-Acetoxy-3-methylpentane-2,4-dione

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Received September 24, 1971

Pyrolysis of 2-acetoxy-2-alkylcyclohexane-1,3-diones (**1–3**) at ~220° for 3–4 hr affords 60–80% of the related 2-alkylcyclopenten-2-ones (**4–6**), plus acetic acid and carbon monoxide.[1,2] It was of interest to see if this remarkably efficient thermal ring contraction reaction could be extended to other types of 2-acetoxy-2-alkyl-1,3-diones. This paper describes the synthesis and pyrolysis of 2-acetoxy-2-methylcyclopentane-1,3-dione (**7**) and 3-acetoxy-3-methylpentane-2,4-dione (**8**). If an analogous ring contraction were to occur, **7** would yield the as yet unreported 2-methylcyclobutenone (**9**) and provide the prototype of a new synthesis of cyclobutenones. The analogous reaction of **8** would yield methyl isopropenyl ketone (**10**) and perhaps provide a useful method for the synthesis of alkyl vinyl ketones.

The preparation of **7** was accomplished by the reaction of 2-methylcyclopentane-1,3-dione (**11**)[3] with lead tetraacetate, in the same manner as the preparations of **2** and **3**,[2] but the maximum yield of pure **7** was only 3%. Exploration of alternate routes, such as thallium triacetate oxidation[4] of enamines **12** and **13**,[5] or epoxidation of enol acetate **14**,[6] in the hope of ther-

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