the corresponding intermediate enol of the tropone reduction (formed from a 1,8 conjugate addition of the reducing agent[8]) tends to ketonize and further reduce.

Amine–boranes are quite stable at low pH and become very effective reducing agents for carbonyl groups in the presence of Lewis acids.[8] However, in the presence of anhydrous HCl, trimethylamine–borane and perhaps dimethylamine–borane react to form trimethylamine–chloroborane. Since both trimethylamine–borane and its chlorinated analog will reduce **2** in the presence of HCl but neither will accomplish the reduction in the absence of acid, the actual reducing agent in our system is not known.

It is interesting that tropone is reduced only with dimethylamine–borane–HCl and does not react with trimethylamine–borane–HCl. This seems to indicate a difference in reduction potential between the two amine–boranes in acidic media.

By successive addition of one-half molar amounts of methanolic HCl it was found that complete reduction of **2** required between one and two molar amounts of HCl. Uv analysis immediately after HCl addition indicated complete reduction.

Prolonged treatment with excess anhydrous HCl (as described in the Experimental Section) tended to decompose product at 0°. However, reduction times up to 1 hr with two molar amounts of methanolic HCl at 0° appeared to have no ill effects on the yield of **1**.

Experimental Section

Reduction of 2,3-Diphenylcyclopropenone (2). Method A. *In Situ* Formation and Reduction of 2.—To a solution of 1,2-diphenyl-3-chlorocyclopropenium aluminum chloridate (**4**, 0.03 mol) in 50 ml of methanol (2% H_2O) at 0° was added 2.10 g of trimethylamine–borane (0.03 mol) in 5 ml of $(CH_2Cl)_2$. The solution was stirred at 0° for 15 min and the solvent was evaporated *in vacuo* at 10°. The residue was suspended in petroleum ether and extracted with ice water. The organic layer was decolorized and cooled on Dry Ice to deposit impurities. The supernatant petroleum ether (bp 35–60°) was then decanted and removed *in vacuo* at 10° to give 3.6 g of **1** (63% yield) melting at 44–47°: nmr ($CDCl_3$) τ 8.48 (1, sharp s) and 2.1–3.0 (5, m); mass spectrum *m/e* (rel intensity) 192 (M^+, 100) and 191 (95); ir (KBr) 1820 cm^{-1}; uv (MeOH) λ_{max} (log ϵ) 228 (3.99), 234 (3.94), 308 (4.14), 318 (4.19), and 336 nm (4.09).[9]

Reduction of Isolated 2. Method B.—To a solution of 1.5 g (0.0073 mol) of **2** in 20 ml of methanol at 0° was added 1.1 g (0.0146 mol) of trimethylamine–borane in 5 ml of $(CH_2Cl)_2$. This solution was acidified with anhydrous HCl over a 2-min period and stirred at 0° for 15 min, and the solvent was evaporated *in vacuo* at 10°. The resulting residue was suspended in petroleum ether and extracted with ice water. The organic layer was decolorized with carbon and stripped *in vacuo* at 10° to give 1.3 g of **1** (91% yield) melting at 44–47° (spectral data identical with above).

Reduction of Isolated 2. Method C.—To a solution of 1.32 g (0.0064 mol) of **2** in 20 ml of methanol at 0° was added 1.1 g (0.0146 mol) of trimethylamine–borane in 5 ml of methanol. This solution was successively acidified with one-half molar equivalents of methanolic HCl (5% solution). After addition of 0.115 g of HCl (0.0032 mol), uv analysis showed partial conversion to **1**. Subsequent additions of one-half molar amounts of methanolic HCl caused immediate increases in the concentration of **1**. Upon addition of a total of 2 molar equiv (0.46 g) of HCl, uv analysis indicated complete disappearance of **2** and **1** as the only evident product. The reaction mixture was allowed to stir for 1 hr at 0° and the solvent was evaporated *in vacuo* at 10°. The resulting residue was suspended in petroleum ether and extracted with ice water. The organic layer was stripped *in vacuo* at 10° to give 1.07 g of **1** (89% yield) melting at 44–49°.

Reduction of Tropone 3.—To a solution of 1.0 g (0.0096 mol) of **3** in 10 ml of CH_2Cl_2 was added 1.0 g (0.0137 mol) of dimethylamine–borane. After treatment with anhydrous HCl over a 2-min period, the solution was stirred at room temperature for 10 min, then extracted with water. The organic layer was separated, dried over molecular sieves, and evaporated *in vacuo* to furnish 0.75 g (71%) of 3,5-cycloheptadienol (**5**). Spectral data (nmr, uv) are consistent with those of Chapman, *et al.*[6]

Registry No.—**1**, 24168-52-3; **2**, 886-38-4; **3**, 539-80-0.

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Asymmetric Reduction of Ketones with (+)-Tris[(*S*)-2-methylbutyl]aluminum Etherate

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Received August 4, 1971

Hydrogen transfer from chiral reducing agents to achiral ketones has been extensively studied in an effort to understand the mechanistic details of asymmetric reduction and in order to develop synthetically useful preparations of optically active secondary carbinols. Reducing agents which have been examined include diisopinocamphenylborane and chiral Grignard reagents, metal alkoxides, and metal hydride complexes.[2] Unfortunately, these reducing agents produce optically active by-products which are often difficult to remove from the desired product. In addition, asymmetric Grignard reductions suffer from the fact that product yield is frequently very low as a result of competing addition and enolization reactions.

In view of the stereospecificity, ease of product isolation, and high yield of product on reduction of ketones with triisobutylaluminum,[3] we have examined the utility of (+)-tris[(*S*)-2-methylbutyl]aluminum etherate as an asymmetric reducing agent. The results of reaction with a series of achiral ketones are indicated in Table I. In each case, the resulting secondary carbinol was obtained easily and in excellent yield with an optical purity similar to that obtained upon reduction of the corresponding ketone with the Grignard reagent derived from (+)-(*S*)-1-chloro-2-methylbutane.[4] The convenience of the experimental procedure and the availability of (+)-tris[(*S*)-2-methylbutyl]aluminum etherate combine to make this an attractive preparation of optically active secondary carbinols.

The preferred transition state, **1**, postulated for the corresponding asymmetric Grignard reduction of ke-

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(2) For a review, see J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, pp 160–218.

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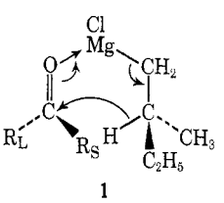
TABLE I
ASYMMETRIC REDUCTION OF KETONES BY (+)-TRIS[(S)-2-METHYLBUTYL]ALUMINUM ETHERATE IN BENZENE SOLUTION

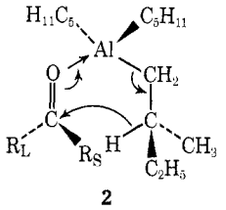
Ketone	Product	Isolated yield, %	$[\alpha]^{25}D$	Configuration	Optical purity, %
Acetophenone	Methylphenylcarbinol	83	−3.38[a]	S[b]	8[c]
Isobutyrophenone	Isopropylphenylcarbinol	93	−14.10[d]	S[e]	30[f]
n-Butyrophenone	*n*-Propylphenylcarbinol	97	−3.39[g]	S[e]	7[h]
3,3-Dimethyl-2-butanone	*tert*-Butylmethylcarbinol	*i*	−0.64[i]	R[k]	13[l]

[a] Determined for the neat liquid. [b] K. Mislow, *J. Amer. Chem. Soc.*, **73**, 3954 (1951). [c] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911). [d] Determined in ether solution, *c* 23.76. [e] R. MacLeod, F. J. Welch and H. S. Mosher, *J. Amer. Chem. Soc.*, **82**, 876 (1960). [f] P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **70**, 355 (1926). [g] Determined in benzene solution, *c* 11.34. [h] J. Kenyon and S. M. Partridge, *J. Chem. Soc.*, 128 (1936). [i] Product isolated by preparative gas chromatography on a 15 ft × 0.25 in. column packed with 10% silicone QF-1 on Chromosorb P; purity >99% by gas chromatography. [j] Determined in absolute ethanol, *c* 7.11. [k] J. Jacobus, Z. Majerski, K. Mislow, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1998 (1969). [l] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 1115 (1914).

tones, positions the larger carbonyl substituent, R_L, opposite the methyl group of the Grignard reagent while the smaller carbonyl substituent, R_S, is opposite the ethyl group.[2] A similar transition state, **2**, would



1



2

be anticipated to control the product stereochemistry in the asymmetric reduction of ketones with (+)-tris-[(*S*)-2-methylbutyl]aluminum etherate.[3a] This model does, in fact, correctly predict the absolute configuration of the predominant enantiomer resulting from reduction of each alkyl phenyl ketone examined. Surprisingly, however, it fails to predict the absolute configuration of the principal enantiomer resulting from reduction of 3,3-dimethyl-2-butanone. Since only one of the three alkyl groups of a trialkylaluminum reagent is utilized in the reduction of ketones,[3b] it appears that the asymmetry of the two alkyl groups not participating in hydride transfer is capable of exerting a controlling influence on the stereochemistry of this reduction.

Experimental Section[5]

(+)-Tris[(*S*)-2-methylbutyl]aluminum Etherate.—Conversion of 34.006 g (0.319 mol) of (+)-(*S*)-1-chloro-2-methylbutane, $[\alpha]^{25}D$ +1.58° (neat), 95% optical purity,[6] to the Grignard reagent followed by reaction with 9.883 g (0.074 mol) of anhydrous aluminum chloride according to the procedure of Pino, *et al.*,[7] afforded 13.882 g (60%) of (+)-tris[(*S*)-2-methylbutyl]-aluminum etherate: bp 111.0–115.0° (3 mm) [lit.[7] bp 87–89° (0.6 mm)]; $[\alpha]^{25}D$ +22.04° (*c* 16.78, hexane).

Reduction of Acetophenone.—The following preparation is representative of the general procedure. Under an atmosphere of dry nitrogen, 1.191 g (10 mmol) of acetophenone was added by syringe to a solution of 3.192 g (10 mmol) of (+)-tris[(*S*)-2-methylbutyl]aluminum etherate in 30 ml of benzene. An immediate orange coloration developed which faded within 30 sec. The solution was heated at reflux under nitrogen for 2 hr. After cooling to room temperature, the resulting mixture was decomposed with 25 ml of 3 *M* HCl and diluted with an additional 30 ml of benzene. The benzene layer was separated, washed with 25 ml of water, and dried over anhydrous $MgSO_4$. Removal of solvent *in vacuo* followed by distillation afforded 1.008 g (83%) of methylphenylcarbinol: bp 77.0–78.0° (4.5 mm); $[\alpha]^{25}D$ −3.38° (neat); >99% pure by gas chromatography on a 15 ft × 0.25 in. column packed with 10% silicone QF-1 on Chromosorb P.

(5) Optical rotations were measured with an O. C. Rudolph and Sons, Inc., Model 200 photoelectric polarimeter equipped with a Model 340 oscillating polarizer.

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Registry No.—(+)-Tris[(*S*)-2-methylbutyl]aluminum etherate, 18902-57-3; acetophenone, 98-86-2; isobutylophenone, 611-70-1; *n*-butyrophenone, 495-40-9; 3,3-dimethyl-2-butanone, 75-97-8; methylphenylcarbinol, 1445-91-6.

Acknowledgment.—Financial support by The Petroleum Research Fund of The American Chemical Society is gratefully acknowledged.

Ring Expansion of 1-Azirines to Azepines *via* Cycloaddition

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Received August 11, 1971

The chemistry of heterotropilidenes has received considerable impetus in recent years due in large part to the elegant synthetic contributions of Paquette and coworkers.[1] In the course of our work on the chemistry of 1-azirines,[2-5] we examined some symmetry-allowed thermal [$\pi^4 + \pi^2$] cycloadditions of the rigid C=N double bond with dienes. We discovered, as reported briefly earlier,[6] that cyclopentadienones reacted readily with 1-azirines (**1**) to furnish in good yields azatropilidenes.

When 2-phenyl-1-azirine (**1a**) was treated with 2,5-dimethyl-3,4-diphenylcyclopentadienone in benzene at reflux temperatures for 4 days, a relatively stable, pale yellow, crystalline compound was isolated in 65% yield. Mass spectral data and elemental analysis were consistent with the molecular formula $C_{26}H_{23}N$. The in-

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(6) A preliminary report of our results was announced in the 15th Annual Report of the Petroleum Research Fund, 1970. After this manuscript was submitted for publication, a communication on the cycloaddition of azirines to cyclopentadieones by D. J. Anderson and A. Hassner appeared in *J. Amer. Chem. Soc.*, **93**, 4339 (1971).