

heated at 100° in a common oil bath overnight. The reactions were found to be complete after 10 hr (incomplete after 2 hr). Each reaction mixture was evaporated down to a small volume and worked up as usual. The product, **15**, from both reactions was shown to be identical by pmr and ir data.

The relative rates of reaction were determined in the same manner as that described for the hydride reduction. Compound **8** reacts *ca.* twice as fast as **7**.

Chromium(II) Chloride Reduction of 5,8,8-Trichlorodibenzobicyclo[3.2.1]octadiene (5).—To a 10-ml flask, flushed with nitrogen gas, was added 0.60 g (1.94 mmol) of **5** and 5 ml of DMF. The flask was capped immediately with a rubber septum. Nitrogen gas was bubbled through the solution of **5** for 30 min. Six milliliters (12 mmol) of Fisher chromium(II) chloride solution (*ca.* 2 M) was injected (*via* syringe) into the solution of **5**, and a dark green color immediately appeared. The reaction solution was diluted with 20 ml of water and extracted twice with 40-ml portions of ether. The combined ether layers were washed with 40 ml of water and dried over anhydrous magnesium sulfate, and the ether was removed by rotary evaporation. A pmr spectrum indicated complete conversion of starting material to **3**. The oil was chromatographed over 10 g of alumina and the fractions were crystallized from carbon tetrachloride to give 400 mg (76% yield) of **3**, mp 119–120°.⁷

Registry No.—**3**, 27995-02-4; **7**, 33065-89-3; **8**, 33065-90-6; **11**, 33065-91-7; **12**, 33065-92-8; **13**, 33065-93-9; **17**, 33065-94-0.

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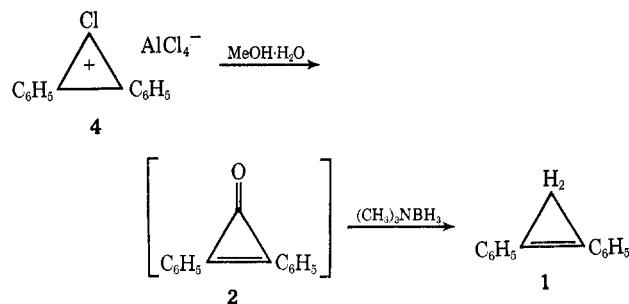
The Reduction of 2,3-Diphenylcyclopropanone and Tropone with Amine-Boranes

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As a possible route to 1,2-diphenylcyclopropene (**1**), the reduction of 2,3-diphenylcyclopropanone (**2**) appeared attractive. Breslow and coworkers^{1,2} have



shown, however, that LiAlH_4 or catalytic reduction of **2** gives dibenzyl ketone, presumably through a diphenylcyclopropanone intermediate. Tropone (**3**), a similar ketone, on reduction with LiAlH_4 gives some

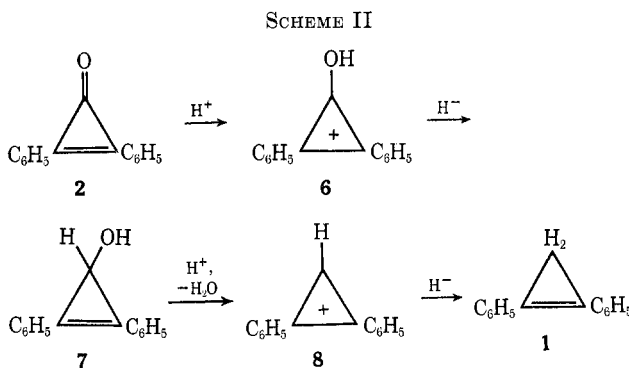
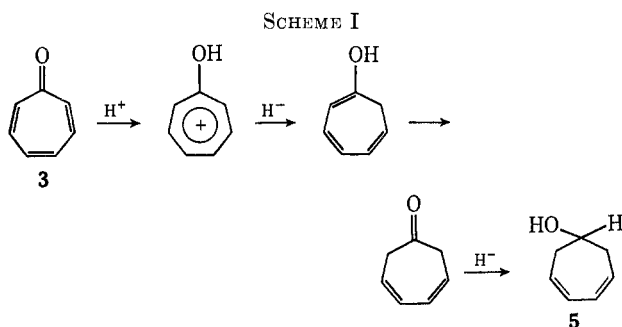
cycloheptatriene, but also 3,4-cycloheptadienol and 3,5-cycloheptadienone.³

We have found that treatment of 1,2-diphenyl-3-chlorocyclopropanone aluminum chloride (**4**)⁴ in a $\text{MeOH} \cdot \text{H}_2\text{O}$ solution (probable *in situ* formation of **2**) with trimethylamine-borane furnishes **1** in 63% yield. Although isolated **2**, when treated with amine-borane, fails to react, **1** is produced in 90% yield upon subsequent treatment of the reduction medium with anhydrous HCl .

It appears, therefore, that the species being reduced in each case is a Lewis acid complex of ketone **2**. Since **3** also forms a molecular complex with HCl ,⁵ its reduction in an acidic medium with amine-borane might be expected to produce cycloheptatriene.

Treatment of **3** with dimethylamine-borane and anhydrous HCl under the reaction conditions, however, gave 3,5-cycloheptadienol (**5**) (the product of a 1,8 conjugate addition)^{5,6} as the sole nonvolatile product in 71% yield.

A possible reason for this difference in the observed products from reduction of these vinylogous ketones is summarized in Schemes I and II.



Scheme II illustrates a reduction route which involves dehydration of an intermediate to form a cyclopropanone cation (**8**) that is easily reduced by amine-borane in the acidic medium.⁷

The difference between the reduction of **2** and **3** (Schemes I and II) probably lies in the tendency of the cyclopropenyl intermediate **7** to dehydrate, whereas

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(2) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).

the corresponding intermediate enol of the tropone reduction (formed from a 1,8 conjugate addition of the reducing agent⁶) 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.³ 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% H₂O) at 0° was added 2.10 g of trimethylamine-borane (0.03 mol) in 5 ml of (CH₂Cl)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 (CDCl₃) 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 (CH₂Cl)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 CH₂Cl₂ 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.

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

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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 diisopinocampheylborane 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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