

Metal Hydride Reductions of *endo*-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (*endo*-Dicyclopentadienone)¹

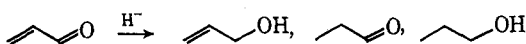
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Reduction of the title compound **1** with aluminum hydride in ether and sodium borohydride in methanol gave exclusively the dienol **2** and the dihydro alcohol **4**, respectively. Reduction with lithium tri-*t*-butoxyaluminum hydride in ether gave predominantly the dihydro ketone **3** while lithium aluminum hydride in ether under various conditions gave mixtures of all three reduction products. Evidence consistent with the formation of a carbon-aluminum bond in the precursor to the dihydro alcohol **4** was obtained by lithium aluminum deuteride reduction. An internally consistent sequence of reactions is proposed to account for the various products.

The reduction of α,β -unsaturated ketones by various metal hydrides can produce an allylic alcohol, a saturated ketone, or a saturated alcohol depending on the substrate, the metal hydride, and the reaction conditions.^{2,3} Brown and Hess^{3w} have recently summarized

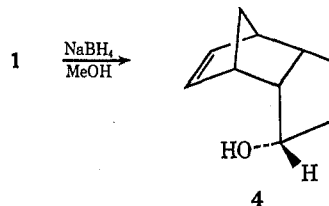
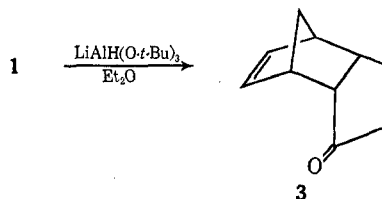
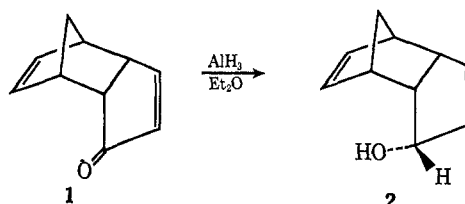
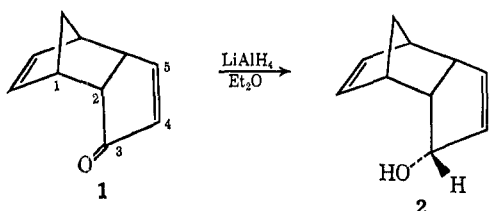


some of the more pertinent data in this area. During the course of our work on reactions in the 1,3-bishomocubyl system,⁴ we carried out the lithium aluminum hydride (LiAlH₄) reduction of the cyclopentenone derivative **1**.⁵ Since appreciable quantities of by-

products in addition to the dienol **2** were formed in some cases, we have examined this reduction in more detail and have examined the use of other metal hydrides.

Results

Reduction of the ketone **1** with aluminum hydride, lithium tri-*t*-butoxyaluminum hydride, and sodium borohydride gave either exclusively or mainly the allylic alcohol **2**, the dihydro ketone **3**, and the dihydro alcohol **4**, respectively. LiAlH₄ reduction of the ketone



(1) For a preliminary report of this work, see W. L. Dilling and R. A. Plepys, *Chem. Commun.*, 417 (1969).

(2) For reviews, see (a) W. G. Brown, *Org. React.*, **6**, 469 (1951); (b) V. M. Micovic and M. L. Mihailovic, "Lithium Aluminum Hydride in Organic Chemistry," Nauka Knjiga, Belgrade, Yugoslavia, 1955; (c) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York, N. Y., 1956, pp 290, 930, 964; (d) W. Klyne, "The Chemistry of Steroids," Methuen and Co. Ltd., London, 1957, p 97; (e) N. G. Gaylord, *J. Chem. Educ.*, **34**, 367 (1957); (f) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 270; (g) C. Djerassi, Ed., "Steroid Reactions," Holden-Day, San Francisco, Calif., 1963, p 135; (h) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 40.

(3) (a) F. A. Hochstein and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3484 (1948); (b) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *ibid.*, **74**, 4223 (1952); (c) F. Sondheimer, M. Velasco, E. Batres, and G. Rosenkranz, *Chem. Ind. (London)*, 1482 (1954); (d) J. K. Norymberski and G. F. Woods, *J. Chem. Soc.*, 3426 (1955); (e) R. Albrecht and C. Tamm, *Helv. Chim. Acta*, **40**, 2216 (1957); (f) C. Djerassi and W. Rittel, *J. Amer. Chem. Soc.*, **79**, 3528 (1957); (g) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959); (h) D. Kupfer, *ibid.*, **15**, 193 (1961); (i) M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962); (j) J. A. Zderic and J. Iriarte, *J. Org. Chem.*, **27**, 1756 (1962); (k) H. C. Brown and P. M. Weissman, *Israel J. Chem.*, **1**, 430 (1963); (l) M. E. Cain, *J. Chem. Soc.*, 3532 (1964); (m) R. C. Cookson, N. S. Isaacs, and M. Szelke, *Tetrahedron*, **20**, 717 (1964); (n) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964); (o) H. C. Brown and P. M. Weissman, *J. Amer. Chem. Soc.*, **87**, 6514 (1965); (p) P. R. Story and S. R. Fahrenholtz, *ibid.*, **87**, 1623 (1965); (q) J. E. Baldwin, *J. Org. Chem.*, **31**, 2441 (1966); (r) H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, **88**, 1464 (1966); (s) P. L. Southwick, N. Latif, B. M. Fitzgerald, and N. M. Zaczek, *J. Org. Chem.*, **31**, 1 (1966); (t) L. A. Paquette and O. Cox, *J. Amer. Chem. Soc.*, **89**, 5633 (1967); (u) E. J. Corey, I. Vlattas, N. H. Andersen, and K. Harding, *ibid.*, **90**, 3247 (1968); (v) J. A. Waters and B. Witkop, *ibid.*, **90**, 758 (1968); (w) H. C. Brown and H. M. Hess, *J. Org. Chem.*, **34**, 2206 (1969); (x) F. G. Cowherd and J. L. von Rosenberg, *J. Amer. Chem. Soc.*, **91**, 2157 (1969).

(4) (a) W. L. Dilling, C. E. Reineke, and R. A. Plepys, *J. Org. Chem.*, **34**, 2605 (1969); (b) W. L. Dilling, R. A. Plepys, and R. D. Kroening, *J. Amer. Chem. Soc.*, **91**, 3404 (1969).

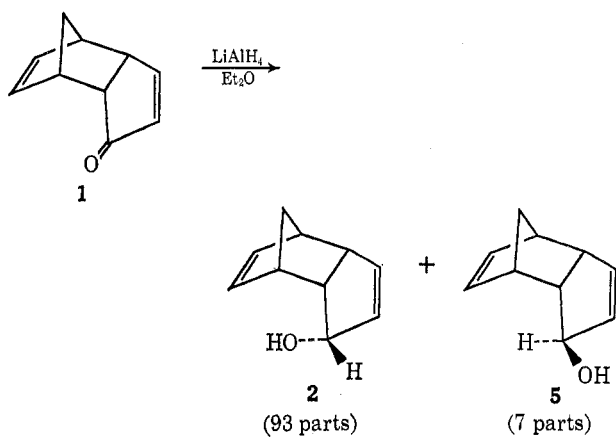
(5) (a) H. Hock and F. Depke, *Chem. Ber.*, **84**, 356 (1951); (b) K. Alder and F. H. Flock, *ibid.*, **87**, 1916 (1954); (c) M. Rosenblum, *J. Amer. Chem. Soc.*, **79**, 3179 (1957).

1 gave mainly carbonyl reduced product **2** along with varying amounts of **3** and **4** depending on the reaction conditions. These results are summarized in Table I. The stereochemistry of these reductions was not studied in detail except for the case of the 0.017 *M* LiAlH₄ reduction to the dienol **2**. In this reaction the ratio of *syn*-hydroxyl product **2** to the epimeric *anti*-hydroxyl product **5** was 93:7. In the other reductions leading to the dienol **2** or the dihydro alcohol **4**, the epimeric purity was not determined. However, in each case the *syn*-hydroxyl products, **2** and **4**, probably were formed in greater than 90% epimeric purity by analogy with the above result and also since spectral data on the products obtained did not indicate any appreciable amounts of the *anti*-hydroxyl epimers.

TABLE I
PRODUCT COMPOSITION FROM METAL HYDRIDE REDUCTIONS
OF *endo*-TRICYCLO[5.2.1.0^{2,6}]DECA-4,8-DIEN-3-ONE (1)

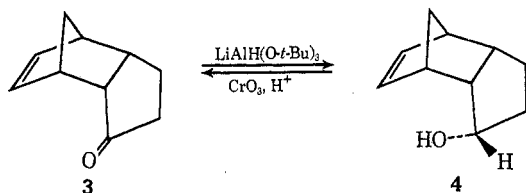
Reducing agent and conditions ^a	Overall yield, %	Product distribution, %		
		2 ^b	3	4
AlH ₃ (3LiAlH ₄ + AlCl ₃) ^c in Et ₂ O ^d	76	100
LiAlH(O- <i>t</i> -Bu) ₃ (LiAlH ₄ + 3 <i>t</i> -BuOH) ^f in Et ₂ O ^d	70	1	83	16
NaBH ₄ in MeOH ^d	72	100
LiAlH ₄ (0.017 M) in Et ₂ O ^b (normal addition) ^d	89	97	...	3
LiAlH ₄ (0.087 M) in Et ₂ O ^b (normal addition) ^d	94	65	17	18
LiAlH ₄ (0.079 M) in Et ₂ O ^b (inverse addition) ⁱ	96	74	26	...

^a More than 2 equiv of hydride/mol of ketone 1 was used in all experiments except that with 0.017 M LiAlH₄ where 1 equiv was used. Reactions carried out either at 0° or *ca.* 25° for 0.5–several hours. ^b Includes any epimeric dieneol 5 which was not separated from 2 by the analytical procedure. ^c Prepared according to the procedure of Jorgenson.^{81,19} ^d Ketone 1 added to hydride solution. ^e Less than 2% by gc analysis. ^f Prepared according to the procedure of Brown and McFarlin.²⁰ ^g Probably less than 5% formed. ^h The initial ketone 1 concentration was 0.067 M. ⁱ Less than 1% by gc analysis. ^j Hydride solution added dropwise over 1 hr to ketone 1 solution.



Attempted reduction of the dienone 1 with LiAlH₄ in hexane as described by Snyder⁶ led to very slight reduction and gave mainly intractable material.⁷

The structures of the ketone 3 and dihydro alcohol 4 were determined by infrared, ultraviolet, nmr, and high-resolution mass spectroscopy (see Experimental Section). In particular, the infrared and ultraviolet spectra of the ketone 3 exhibited bands characteristic of a cyclopentanone derivative.⁸ Further structural evidence for 3 and 4 was provided by lithium tri-*t*-butoxyaluminum hydride reduction of the ketone 3 to 4 and



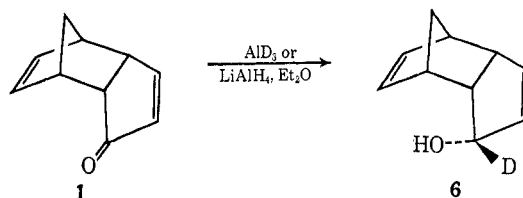
(6) E. I. Snyder, *J. Org. Chem.*, **32**, 3531 (1967).

(7) Use of hexane as the solvent prevents reduction of the double bond in methyl cinnamate.⁶

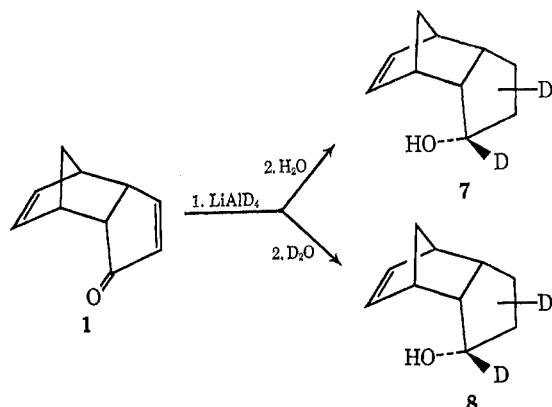
(8) (a) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 202; (b) W. D. Kumler and A. C. Huitric, *J. Amer. Chem. Soc.*, **78**, 3369 (1956).

reconversion of the alcohol 4 to 3 by Jones oxidation.⁹ The reduction of 3 to 4 would be expected to proceed *via* hydride attack from the *exo* side of the carbonyl group and produce the *endo* alcohol 4 as the major product.^{3p,w,10} The relative nmr chemical shifts of the proton on the hydroxyl-bearing carbon atom (–CHOH–) of the alcohols 2, 4, and 5^{3g} are in agreement with this assignment. This proton in the *anti*-dieneol 5 (–3.96 ppm) is shielded with respect to the corresponding proton of the *endo*-dieneol 2 (–4.59 ppm), probably owing mainly to the anisotropy of the C-1–C-2 single bond. The chemical shift for this proton in the dihydro alcohol 4 is –4.29 ppm as expected when the double bond is saturated. The chemical shift of the corresponding proton of the epimer of 4 would be expected to be *ca.* –3.7 ppm.

Reduction of the dienone 1 with aluminum deuteride or lithium aluminum deuteride (LiAlD₄) gave the expected monodeuterated dieneol 6. The dihydro alcohol



7 produced in the LiAlD₄ reaction under conditions which maximized its yield (entry 5, Table I) contained two deuterium atoms as shown by mass spectrometry. Hydrolysis with deuterium oxide gave a trideuteriodieneol 8. In both cases nmr analysis indicated that one



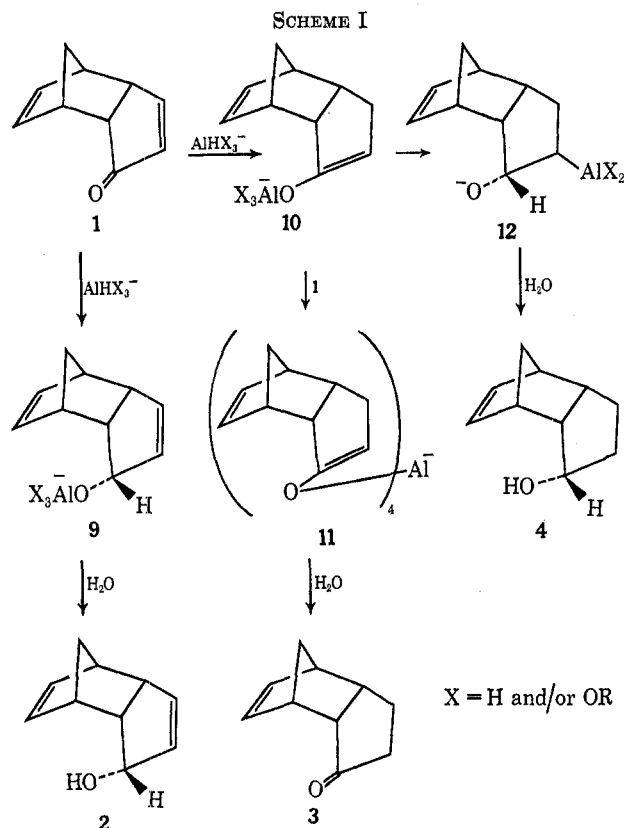
of the deuterium atoms was on C-3 while the others were on one or more of the secondary carbon atoms, presumably C-4 and C-5. The O–D was washed out with ordinary water.

Discussion

A reaction sequence consistent with these results is shown in Scheme I. The ketone 1 apparently undergoes both 1,2 and 1,4 reduction by LiAlH₄ to give intermediates 9 and 10, respectively. In contrast to the LiAlH₄ reduction of cinnamaldehyde, where an alkoxyaluminum hydride from cinnamyl alcohol is an intermediate in the formation of the dihydro alcohol, hydro-

(9) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lenin, *J. Chem. Soc.*, 2548 (1953).

(10) C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).



cinnamyl alcohol,^{8a,i} the allylic alcohol 2 is inert to the reaction conditions.

The enolate 10 can undergo either further reaction with ketone 1 to give ultimately the tetraalkoxyaluminum ion 11, or intramolecular aluminum hydride addition to the double bond to give the alkylaluminum species 12. Alternatively, the latter reaction could be replaced by an intermolecular reaction of an aluminum hydride species with the keto tautomer of 10. The intramolecular transformation of 10 to 12 is somewhat analogous to the LiAlH_4 reduction of an enol acetate to a saturated alcohol described by Dauben and Eastham.¹¹ The ordinary water and deuterium oxide hydrolysis of the salt produced by reaction with LiAlD_4 is consistent with the formation of a carbon aluminum bond in 12.

The absence of any carbon-carbon double-bond reduction of 1 by aluminum hydride is readily explained as due to initial coordination of the electrophilic aluminum hydride to the carbonyl oxygen atom and hydride transfer to the carbonyl carbon atom.⁸ⁱ The other nucleophilic reducing agents in Table I apparently can transfer a hydride ion to the 5 position in a manner analogous to a Michael addition.

Tri-*t*-butoxyaluminum hydride attacks ketone 1 almost exclusively at C-5, possibly for steric reasons, and leads to a tetraalkoxy species 10 which on hydrolysis gives only ketone 3. The small amount of dihydro alcohol 4 may arise from attack on the enolate 10 or its keto tautomer by another aluminum hydride ion. Since the ketone 3 reacts readily with lithium tri-*t*-butoxyaluminum hydride to give alcohol 4, the ketone 3 must not be formed until after hydrolysis. Story and Fahrenholtz^{8p} and Brown and Hess^{3w} have reported

(11) W. G. Dauben and J. E. Eastham, *J. Amer. Chem. Soc.*, **70**, 3484 (1948).

analogous results with similar cyclopentenone derivatives.

Contrary to expectation,^{2h} sodium borohydride also leads almost exclusively to initial 1,4 reduction which produces the boron analog of 10. Owing to the protic solvent, this intermediate is converted to ketone 3 which in turn is reduced to the dihydro alcohol 4. The results of Brown and Hess^{3w} are completely in accord with this reaction.¹²

The amounts of 1,2 and 1,4 reduction of 1 with LiAlH_4 are apparently concentration dependent with higher hydride concentrations favoring 1,4 reduction. The relatively large amount of 1,4 reduction obtained with inverse addition, conditions which should lead to a very low hydride concentration, may be due to a very rapid reaction in the vicinity of the concentrated hydride solution as it contacts the ketone solution. This concentration dependence could be due to the 1,4 reduction's having a higher order dependence on hydride concentration than the 1,2 reduction has. Alternatively, aggregation of the LiAlH_4 in ether could account for the concentration dependence.¹³ With a low ketone 1 concentration (normal addition), the conversion of intermediate 10 to 12 is competitive with further reaction of 10 with ketone 1. At a high ratio of ketone 1 to LiAlH_4 (inverse addition), the reaction of 10 with excess ketone 1 wins out leading to relative large amounts of ketone 3. The predominant formation of the *syn*-hydroxyl epimers, 2 and 4, is expected on the basis of steric approach control.^{10,16}

Experimental Section

General.—Melting points were determined in capillary tubes and are corrected. Infrared spectra were recorded using a Perkin-Elmer 337 double grating spectrometer by Mr. F. L. Beman and coworkers. The ultraviolet absorption spectra were obtained by Mr. Beman and coworkers with a Perkin-Elmer 202 ultraviolet-visible spectrophotometer. Nuclear magnetic resonance (nmr) spectra were obtained by Mr. Beman and coworkers with a Varian A-60 spectrometer. Chemical shifts are reported in parts per million (δ) relative to internal TMS. Mass spectral analyses were performed by Dr. L. A. Shadoff, Mrs. W. L. Dilling, and Miss W. J. Plagens on either a magnetically scanning 90° sector spectrometer using an electron ionizing voltage of 75 eV and a vaporizer temperature of 200° (unless specified otherwise), or an Atlas CH4B (EFO4B ionization source) with direct probe sample introduction, or a high-resolution Consolidated Electro-dynamics 21-110B spectrometer. Microanalyses were determined by Mr. L. E. Swim and coworkers. Gas chromatographic (gc) analyses were performed with a F & M 500 gas chromatograph using a 10 ft \times 0.25 in. column packed with 20% Apiezon L on acid-washed Chromosorb W at 150° with a helium flow rate of 150 ml/min unless specified otherwise. Under these conditions, the retention times of the reduction products were 14.0 min, 2;

(12) Brown and Hess^{3w} reported that reduction of *endo*-tricyclo[5.2.1.0^{2,6}]dec-4-en-3-one with sodium borohydride in refluxing ethanol gave 100% *endo, syn*-tricyclo[5.2.1.0^{2,6}]decan-3-ol while Cowherd and von Rosenberg^{3x} reported that reduction of the same ketone with sodium borohydride under unspecified conditions gave *endo, syn*- and *endo, anti*-tricyclo[5.2.1.0^{2,6}]dec-4-en-3-ol in a 9:1 ratio, respectively.

(13) The degree of association [n of $(\text{LiAlH}_4)_n$] was 1.58 at 0.05 M, 2.27 at 0.5 M, 2.85 at 1.0 M, and 3.64 at 2.0 M as determined by boiling point elevation in diethyl ether.¹⁴ Wiberg¹⁵ reported that 0.08 M LiAlH_4 in ether is dimeric and that at 0.8 M it is trimeric.

(14) C. B. Roberts, Dow Chemical Co., private communication.

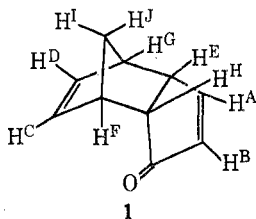
(15) E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).

(16) Brown and Hess^{3w} reported 100% *anti* attack by sodium borohydride on *endo*-tricyclo[5.2.1.0^{2,6}]dec-4-en-3-one. Rothberg¹⁷ reported 99% *anti* attack on *endo*-tricyclo[5.2.1.0^{2,6}]decan-3-one by LiAlH_4 . Replacement of the *endo* hydrogen atoms at C-8 and C-9 by the C-8-C-9 double bond as in 1 and 3 should lead to slightly increased ease of *syn* attack by the hydride.

(17) I. Rothberg, unpublished results quoted by H. C. Brown and W. J. Hamor, *J. Amer. Chem. Soc.*, **89**, 1524 (1967).

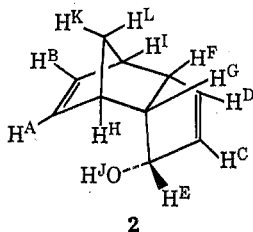
17.0 min, **3**; 18.2 min, **4**. Compounds **3** and **4** were not completely resolved. Operation of the column at higher temperature caused partial decomposition of the dienol **2**. The *anti*-hydroxy epimer **5** was not separated from **2** under the gc conditions used. Product distributions were determined from gc peak areas (height times width at half-height) assuming equal thermal conductivities on a molar basis.

endo-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (1).—This ketone was prepared according to the chromic acid oxidation procedure of Alder and Flock^{5b} as modified by Woodward and Katz.^{3g} Material for the following experiments was purified by vacuum sublimation at 110° (0.5 mm) and recrystallization from hexane, mp 59–63°. A more highly purified sample for spectral data was obtained by recrystallization four more times from hexane (1% impurity by gc): mp 65.5–67.5° (lit. mp 58–59°,¹⁸ 58–60°,^{3a} 59.0–59.5°,^{5c} 65.3–65.6°,^{3g} 80°^{5b}); $\nu_{\max}^{\text{CCl}_4}$ 3075 (w) and 3055 (w) (=C—H), 2980 (s), 2945 (m) and 2880 (m) (C—H), 1715 (vs, C=O), 1585 (s, C=C) cm⁻¹; $\nu_{\max}^{\text{CS}_2}$ 723 (s, *cis* H's) cm⁻¹; $\lambda_{\max}^{\text{hexane}}$ 218.5 m μ (ϵ 8890, $\pi \rightarrow \pi^*$), 314 (sh, 17.0), 327 (26.8), 341.5 (32.3, $n \rightarrow \pi^*$), 358 (25.5), 376 (9.6); $\lambda_{\max}^{\text{MeOH}}$ 226.5 m μ (ϵ 7420, $\pi \rightarrow \pi^*$), 321.5 (36.1, $n \rightarrow \pi^*$); nmr spectrum (CCl₄) a doublet of doublets centered at -7.25 (H^A, 1.0 H, $J_{AB} = 5.7$, $J_{AE} = 2.6$ cps), a multiplet at -6.0 to -5.6 (H^{B,C,D}, 2.9 H), an eight-line



multiplet centered at -3.36 (H^E, $J_{EH} \sim 5.5$, $J_{EG} = 4.1$, $J_{AE} = 2.6$ cps) overlapping with a multiplet at -3.3 to -3.05 (H^F or G) (2.0 H total), a multiplet at -3.05 to -2.8 (H^G or F, 1.0 H), an unsymmetrical doublet of doublets centered at -2.68 (H^H, 1.1 H, $J_{EH} = 5.4$, $J_{FH} = 4.9$ cps), and an unsymmetrical doublet of triplets centered at -1.77 (H^I or J, $J_{IJ} = 8.4$, $J_{FI} \approx J_{GI}$ or $J_{FJ} \approx J_{GJ}$ or $J_{FI} \approx J_{GI} = 1.6$ cps) overlapping with another unsymmetrical doublet of triplets centered at -1.57 ppm (H^J or I, $J_{IJ} = 8.5$, $J_{FJ} \approx J_{GJ}$ or $J_{FI} \approx J_{GI} = 1.4$ cps) (2.0 H total); mass spectrum *m/e* 39 (relative intensity 23.1, C₂H₃⁺), 40 (10.9, C₂H₄⁺), 51 (14.9, C₂H₅⁺), 65 (26.2, C₂H₅⁺), 66 (81.5, C₂H₆⁺), 77 (10.3, C₆H₅⁺), 78 (14.0, C₆H₆⁺), 91 (28.2, C₇H₇⁺), 103 (17.1, M⁺ - C₂H₂O or C₂H₇), 115 (31.3, M⁺ - CH₃O), 117 (100.0, M⁺ - CHO or C₂H₅), 118 (50.6, M⁺ - CO or C₂H₄), 131 (19.8, M⁺ - CH₂), 132 (11.4, M⁺ - CH₂), 146 (27.5, M⁺) (some relative intensities variable).

endo,syn-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol (2).—Material prepared by the lithium aluminum hydride (0.063 M in ether) reduction of the dienone **1**, according to the procedure of Woodward and Katz,^{3g} was purified by recrystallization four times from pentane and sublimation at 60° (0.15 mm): mp 82.5–85° (lit. mp 85.0–85.5°,^{3a} 85.0–85.8°^{3g}); $\nu_{\max}^{\text{CCl}_4}$ 3620 (m, free O—H), 3500 (m, br, bonded O—H), 3060 (m, =C—H), 2975 (s) and 2945 (s), 2910 (m) and 2880 (m) (C—H), 1625 (w, cyclopentenyl C=C), 1585 (w, norbornenyl C=C) cm⁻¹; $\nu_{\max}^{\text{CS}_2}$ 728 (s, *cis* H's) cm⁻¹; nmr spectrum (CCl₄) an unsymmetrical doublet of doublets centered at -6.11 (1.0 H, H^A or B, $J_{AB} = 5.6$, J_{AH} or $BI = 2.5$ cps), an unsymmetrical doublet of doublets centered at -5.68



(H^B or A, $J_{AB} = 5.6$, J_{BI} or $AH = 3.1$ cps) overlapping with a singlet at -5.50 (H^C, H^D) (2.9 H total), a doublet of doublets (with further splitting evident) centered at -4.59 (1.0 H, H^E, $J_{EG} = 8.5$, $J_{CE} = 1.1$ cps), an unsymmetrical doublet of doublets centered at -3.23 (1.0 H, H^F, $J_{FG} = 7.3$, $J_{FI} = 4.1$ cps), a

multiplet at -3.1 to -2.6 with a maximum at -2.87 (3.0 H, H^G, H^H, H^I), a singlet at -2.06 which disappeared on shaking the solution with D₂O (1.0 H, H^J), and two overlapping unsymmetrical doublets of triplets centered at -1.55 (H^K or L, $J_{KL} = 8.0$, $J_{HK,IK}$ or $HL,IL = 1.6$ cps) and -1.36 ppm (H^I or K, $J_{KL} = 8.0$, $J_{HL,IL}$ or $HK,IK = 1.4$ cps) (2.1 H total); mass spectrum (150°) *m/e* 39 (11.3, C₂H₃⁺), 66 (100.0, C₂H₆⁺), 82 (36.1 C₂H₅O⁺), 91 (12.8, C₇H₇⁺), 115 (16.0, M⁺ - CH₃O), 117 (24.1, M⁺ - CH₃O), 129 (16.5, M⁺ - H₂O), 130 (51.2, M⁺ - H₂O), 148 (4.3, M⁺).

Aluminum Hydride Reduction of Dienone 1.—A slurry of aluminum hydride in ether was prepared according to the procedure of Jorgenson.^{31,19} To a stirred mixture of 0.38 g (10 mmol) of lithium aluminum hydride in 50 ml of dry ether there was added 0.4 g (3 mmol) of aluminum chloride in small portions. To this stirred slurry of aluminum hydride and lithium chloride, the ketone **1** (0.50 g, 3.4 mmol) was added dropwise as a solution in 10 ml of ether. After stirring for 0.5 hr at ca. 25°, the reaction mixture was hydrolyzed by the cautious addition of 5 ml of water, followed by 15 ml of 5 N hydrochloric acid. The ether layer was separated, washed with water, and dried (MgSO₄). Evaporation of the solvent and sublimation of the residue at 100° (0.5 mm) afforded 0.38 g (76%) of *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-*syn*-3-ol (**2**), mp 62–72°. One recrystallization from hexane gave 0.28 g of alcohol, mp and mp 63–65°. The infrared and nmr spectra of this product were identical with those of an authentic sample. Analysis by gc also showed only one component. The estimated limit of gc detection for the dihydro ketone **3** and dihydro alcohol **4** was ca. 2%.

Aluminum Deuteride Reduction of Dienone 1.—A slurry of aluminum deuteride was prepared by the addition of 1.8 g (13.5 mmol) of aluminum chloride to a stirred, cold (-30°) mixture of 1.5 g (40 mmol) of lithium aluminum deuteride in 500 ml of dry ether. The stirred mixture was warmed to ca. 25° and 15.0 g (103 mmol) of ketone **1** in 90 ml of ether was added dropwise over a period of 0.5 hr. After stirring at ca. 25° for 18 hr, the hydride solution was decomposed by the dropwise addition of 10 ml of water, followed by 100 ml of dilute sulfuric acid. The ether layer was separated, washed with water, and dried (MgSO₄). Evaporation left a thick yellow oil which, after sublimation at 100° (0.5 mm), afforded 9.0 g (60%) of a white waxy solid. Recrystallization from hexane gave 3.8 g of crystalline solid, mp 56–58°. The infrared and nmr spectra of this sample were nearly identical with those of the deuterated dienol **6** described below. Gc analysis indicated less than 5% impurities.

Lithium Tri-*t*-butoxyaluminum Hydride Reduction of Dienone 1. Preparation of *endo*-Tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (3). A slurry of lithium tri-*t*-butoxyaluminum hydride²⁰ was prepared by the dropwise addition of 3.50 g (43.3 mmol) of *t*-butyl alcohol to a stirred mixture of 0.60 g (15.8 mmol) of lithium aluminum hydride in 125 ml of dry ether. To this mixture was added a solution of the dienone **1** (1.00 g, 6.85 mmol) in 3 ml of ether. After stirring at room temperature for 16 hr, the mixture was hydrolyzed by the dropwise addition of 5 ml of water, followed by 25 ml of 5 N hydrochloric acid. The ether layer was separated, washed with water, and dried (MgSO₄). Evaporation of the solvent gave 0.70 g (70%) of a colorless oil, which by gc analysis had the composition shown in Table I.

Repetition of the above experiment with 1.90 g (29 mmol) of *t*-butyl alcohol, 0.30 g (8 mmol) of lithium aluminum hydride, and 0.50 g (3.4 mmol) of ketone **1** in 100 ml of ether, followed by the usual work-up and sublimation at 100° (0.5 mm), gave 0.20 g (40%) of the ketone **3**: mp 100–103°; $\nu_{\max}^{\text{CCl}_4}$ 3070 (w, =C—H), 2970 (s), 2950 (s), and 2875 (m) (C—H), 1740 (s, C=O) cm⁻¹; $\nu_{\max}^{\text{CS}_2}$ 730 (s, *cis* H's) cm⁻¹; $\lambda_{\max}^{\text{n-hexane}}$ 273 m μ (sh, ϵ 15.8), 284 (sh, 21.0), 295.5 (26.4), 305.5 (27.4, $n \rightarrow \pi^*$), 317 (21.1), 329 (sh, 9.8); $\lambda_{\max}^{\text{MeOH}}$ ~290 m μ (sh, ϵ 29.6); nmr spectrum (CDCl₃) a multiplet at -6.4 to -5.9 with a maximum at -6.18 (1.9 H, =C—H), a multiplet at -3.3 to -2.55 with a maximum at -2.93 (4.0 H, >C—H), and a multiplet at -2.55 to -1.1 with maxima at -2.05 and -1.47 ppm (6.1 H, -CH₂-).

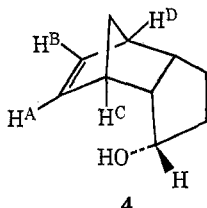
Anal. Calcd for C₁₀H₁₂O: nuclidic mass, 148.0888. Found: nuclidic mass, 148.0874.

Sodium Borohydride Reduction of Dienone 1. Preparation of *endo,syn*-Tricyclo[5.2.1.0^{2,6}]dec-8-en-3-ol (4).—To a solution of 0.75 g (20 mmol) of sodium borohydride in 20 ml of methanol at

(19) See also, A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1999 (1947).

(20) H. C. Brown and R. F. McFarlin, *ibid.*, **80**, 5372 (1958).

0°, there was added dropwise a solution of 2.5 g (17 mmol) of ketone 1 in 5 ml of methanol. The solution was stirred at 0° for 0.5 hr and at *ca.* 25° for 2 hr. The methanol solution was evaporated under vacuum to *ca.* one-half its original volume and hydrolyzed by stirring with 10 ml of 5 *N* hydrochloric acid for 15 min. The reaction mixture was diluted with 100 ml of water and extracted with two 50-ml portions of ether. The combined extracts were washed with water and dried (MgSO₄). After evaporation of the solvent, the residue was sublimed at 100° (0.5 mm) to give 1.8 g (72%) of a waxy solid. The sublimate was re-sublimed and recrystallized from hexane to give 1.05 g of alcohol 4: mp 134.5–137.5°; $\nu_{\text{max}}^{\text{CCl}_4}$ 3640 (w) and ~3350–3250 (w) (O—H), 3070 (w, =C—H), 2970 (s), 2940 (s), and 2875 (m) (C—H) cm⁻¹; $\nu_{\text{max}}^{\text{CS}_2}$ 737 (s, *cis* H's) cm⁻¹; nmr spectrum (CDCl₃) an unsymmetrical doublet of doublets centered at -6.30 (H^A or B, $J_{AB} = 5.5$, J_{AC} or $J_{BD} = 2.6$ cps) overlapping with another



unsymmetrical doublet of doublets at -6.12 (H^B or A, $J_{AB} = 5.8$, J_{BD} or $J_{AC} = 2.8$ cps) (2.0 H total), an approximate quartet ($J \sim 7$ cps) centered at -4.3 superimposed on a multiplet at -4.5 to -4.0 (1.0 H, >CHOH-), a multiplet at -3.1 to -2.5 with a maximum at -2.81 (4.0 H, -C—H), and a multiplet at -2.1 to -1.1, with a maximum at -1.42, overlapping with a singlet at -1.93 ppm (~1.1 H, O—H) (7.1 H total, -CH₂-); mass spectrum m/e 132.0947 (M⁺ - H₂O, calcd for C₁₀H₁₂⁺ 132.0939), 150 (M⁺).

Anal. Calcd for C₁₀H₁₄O: C, 79.96; H, 9.39; nuclidic mass, 150.1047. Found: C, 79.78; H, 9.38; nuclidic mass, 150.1053.

Repetition of this reaction under essentially the same conditions and analysis of the crude reaction mixture by gc (10 ft × 0.25 in. 20% XE-60 silicone nitrile on 60–80 mesh Gas-Chrom Z, 175°, He flow rate 75 ml/min) showed only a single product 4, t_R 18.2 min.

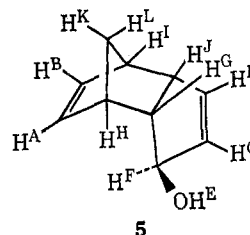
Lithium Aluminum Hydride Reduction of Dienone 1. A. 0.087 *M* Hydride.—The solid ketone 1 (150 mg, 1.0 mmol) was added in one portion to a stirred slurry of 50 mg (1.3 mmol) of lithium aluminum hydride in 15 ml of dry ether (0.087 *M*). The reaction mixture was stirred at *ca.* 25° for 1 hr and hydrolyzed by the successive addition of 0.1 ml of water, 0.2 ml of 15% sodium hydroxide, and 0.3 ml of water. The hydrolyzed solution was stirred for 1 hr, the ether layer was decanted, and the etheral precipitate was washed with fresh ether. The combined ether solutions were dried (MgSO₄) and concentrated to *ca.* 3 ml; 50 mg of *o*-dichlorobenzene was added as an internal standard for gc analysis. The results of this analysis are given in Table I.

B. 0.017 *M* Hydride.—To a stirred slurry of 10 mg (0.26 mmol) of lithium aluminum hydride in 15 ml of dry ether (0.017 *M*), 150 mg (1.0 mmol) of ketone 1 was added in one portion. The reaction mixture was stirred at *ca.* 25° for 1 hr and hydrolyzed by adding 0.05 ml of water, 0.1 ml of 15% sodium hydroxide, and 0.2 ml of water. Further work-up and analysis as in part A gave the results shown in Table I.

A similar reaction was carried out by adding a solution of the ketone 1 (0.50 g, 3.4 mmol, free of the precursor dienol 5) in several milliliters of dry ether to a stirred slurry of lithium aluminum hydride (0.133 g, 3.5 mmol) in 200 ml of dry ether (0.017 *M*) at 22° and stirring for 1 hr. Work-up as described above with evaporation to dryness gave 0.42 g (83%) of a white solid whose nmr spectrum indicated a composition of 93% 2 and 7% 5, based on integration of the -CHOH- peaks at -4.59 and -3.96 ppm, respectively. The infrared spectrum was also consistent with this composition and indicated the presence of a small amount of the dihydro ketone 3, as evidenced by the appearance of medium-weak bands at *ca.* 1740 and 1168 cm⁻¹.

An authentic sample of the *anti*-hydroxydienol 5, bp 73–74° (0.8–0.5 mm), was prepared according to the selenium dioxide oxidation procedure of Woodward and Katz.²⁸ Spectral data: $\nu_{\text{max}}^{\text{CCl}_4}$ 3620 (w, free O—H), 3330 (m, br, bonded O—H), 3060 (m, =C—H), 2970 (s), 2940 (s), 2900 (m) and 2875 (m)

(C—H), 1625 (w, cyclopentenyl C=C), 1580 (w, norbornenyl C=C) cm⁻¹; $\nu_{\text{max}}^{\text{CS}_2}$ 730 (s, *cis* H's) cm⁻¹; nmr spectrum (CCl₄) a multiplet at -6.0 to -5.8 with a maximum at -5.85 (2.0 H,



two of four olefinic protons) overlapping with a multiplet at -5.8 to -5.4 with a maximum at -5.61 (2.1 H, remaining two olefinic protons), a singlet at -4.38 (1.0 H, H^E), a multiplet at -4.05 to -3.9 with a maximum at -3.96 (1.0 H, H^F), a multiplet at -3.5 to -3.1 (1.0 H, H^G or J), a multiplet at -3.1 to -2.9 centered at -3.00 (1.0 H, H^H or I), a multiplet at -2.9 to -2.6 with a maximum at -2.75 (1.0 H, H^I or H), an eight line multiplet centered at -2.49 (0.9 H, H^J or G, $J_{GJ} = 7.8$, J_{IJ} or $J_{GH} = 4.6$, J_{DJ} or $J_{FG} = 2.1$ cps), and two overlapping unsymmetrical doublets of triplets centered at -1.66 (H^K or L, $J_{KL} = 8.0$, $J_{HK,IK}$ or $J_{HL,IL} = 1.7$ cps), and -1.34 ppm (H^L or K, $J_{KL} = 8.0$, $J_{HL,IL}$ or $J_{HK,IK} = 1.4$ cps), (2.0 H total); mass spectrum m/e 66 (C₅H₆⁺), 82 (C₆H₆O⁺), 130 (M⁺ - H₂O), 148 (M⁺).

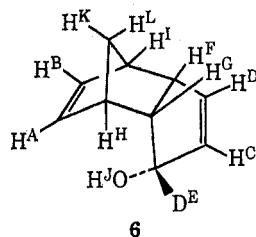
C. Inverse Addition, 0.079 *M* Hydride.—A solution of lithium aluminum hydride was prepared by stirring a slurry of 0.15 g (4.0 mmol) of lithium aluminum hydride and 50 ml of dry ether (0.079 *M*) for 2 hr at *ca.* 25°. This mixture was then filtered into a dry addition funnel, and the hydride solution was added dropwise to a stirred, cold (0–5°) solution of 0.50 g (3.4 mmol) of ketone 1 in 50 ml of dry ether (0.068 *M*). The addition was carried out over a period of 1 hr and the reaction mixture was then stirred at *ca.* 25° for 0.5 hr. Hydrolysis was accomplished by adding 1 ml of water, 1 ml of 15% sodium hydroxide, and 3 ml water. The granular solids were filtered and washed with fresh ether, and the combined ether solutions were dried (MgSO₄). Concentration and gc analysis showed the results given in Table I. Evaporation of all the ether left 0.48 g (96%) of a colorless oil.

Lithium Aluminum Deuteride Reduction of Dienone 1. A. Hydrolysis with Water.—A solution of the ketone 1 (0.3 g, 2 mmol) in 1 ml of dry ether was added to a stirred slurry of lithium aluminum deuteride (0.2 g, 4.8 mmol) in 20 ml of ether over a period of 0.5 min. After stirring at *ca.* 25° for 0.5 hr, 1 ml of water was added cautiously, followed by 5 ml of 5 *N* hydrochloric acid. The ether layer was separated, washed with water, and dried. The dihydro alcohol 7 was isolated by preparative gc (Apiezon L column described above, 225°, He flow rate 40 ml/min, t_R 9.9 min): mp 131–133°; nmr spectrum (CDCl₃) multiplets centered at -6.2 (1.5 H, =C—H), -4.3 (0.4 H, -CHOH-), -2.8 (4.0 H, >C—H), and -1.5 ppm (6.2 H, -CH₂- and OH); mass spectrum m/e 152, M⁺, C₁₀H₁₂D₂O⁺.

B. Hydrolysis with Deuterium Oxide.—This reaction was carried out as described in part A except that 1 ml of deuterium oxide was substituted for the 1 ml of water used for the hydrolysis. The dihydro alcohol 8 was isolated by preparative gc as above: mp 132–133°; nmr spectrum multiplets at -6.2 (1.5 H, =C—H), -4.3 (0.2 H, -CHOH-), -2.8 (4.0 H, >C—H), and -1.5 ppm (5.2 H, -CH₂- and OH); mass spectrum m/e 153, M⁺, C₁₀H₁₁D₃O⁺.

C. Preparation of *endo*-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-*syn*-3-ol (6).—A solution of the dienone 1 (25.6 g, 0.175 mol) in 200 ml of dry ether was added over a period of 1 hr to a stirred suspension of lithium aluminum deuteride (3.1 g, 0.074 mol) in 1 l. of dry ether at 26–28°. After stirring for another 20 min, 3.1 ml of water were added with external cooling, followed by 3.1 ml of 15% aqueous sodium hydroxide and 9.3 ml of water. The mixture was filtered and the ether was removed from the filtrate under vacuum to give 26.5 g of white solid. Recrystallization from hexane gave 19.0 g (73%) of white crystalline dienol 6, mp 75–85°. A 2.0-g portion was recrystallized twice from pentane and sublimed three times at 60° (0.15 mm) to give 1.08 g (39%) of the analytical sample of 6: mp 86.5–87.5°; $\nu_{\text{max}}^{\text{CCl}_4}$ 3615 (m, free O—H), 3500 (m, br, bonded O—H), 3060 (m, =C—H), 2975 (s), 2940 (s), 2910 (m) and 2880 (m) (C—H), 2225 (w), 2185 (w), 2155 (w), and 2135 (w) (C—D), 1625 (w, cyclopentenyl C=C), 1585 (w, norbornenyl C=C) cm⁻¹; $\nu_{\text{max}}^{\text{CS}_2}$ 732 (s, *cis* H's)

cm⁻¹; nmr spectrum (CCl₄) an unsymmetrical doublet of doublets centered at -6.12 (1.1 H, H^A or B, $J_{AB} = 5.7$, J_{AH} or $BI = 2.2$ cps), an unsymmetrical doublet of doublets centered at



-5.68 (H^B or A, $J_{AB} = 5.7$, J_{BI} or $AH = 3.0$ cps) overlapping with a singlet at -5.51 (H^C, H^D) (2.8 H total), an unsymmetrical doublet of doublets centered at -3.24 (1.0 H, H^F, $J_{FG} = 7.9$, $J_{FI} = 4.0$ cps), a multiplet at -3.1 to -2.5 with a maximum at -2.91 (3.1 H, H^G, H^H, H^I), a singlet at -2.15 (0.9 H, H^J), and two overlapping unsymmetrical doublets of triplets centered at -1.55 (H^K or L, $J_{KL} = 8.0$, $J_{HK,IK}$ or $HL,IL = 1.7$ cps) and -1.36 ppm (H^L or K, $J_{KL} = 8.1$, $J_{HL,IL}$ or $HK,IK = 1.4$ cps) (2.1 H total), no absorption detected in the -5.0 to -4.0 ppm region for H^E; mass spectrum (200°) *m/e* 66 (100.0, base peak, C₆H₆⁺), 83 (56.1, C₆H₅DO⁺), 91 (0.72, C₇H₇⁺), 92 (0.68, C₇H₆D⁺), 117 (1.6, M⁺ - CH₂DO), 130 (1.3, M⁺ - HDO), 131 (2.5, M⁺ - H₂O), 149 (very weak, M⁺) 150 (0.22, M⁺ + H).

Anal. Calcd for C₁₀H₁₁DO: C, 80.50; H (D), 8.78. Found: C, 80.5; H (D), 8.31.

Stability of Dienol 2 to Lithium Aluminum Hydride.—The dienol 2 (50 mg) was added to a slurry of lithium aluminum hydride (100 mg) in 5 ml of dry ether and allowed to stand at ca. 25° for 18 hr. After hydrolysis with water and dilute hydrochloric acid, separation of the aqueous layer, washing with water, and concentration of the ether solution, gc analysis showed only starting material.

Chromic Acid Oxidation of Dihydro Alcohol 4.—To a cold (10–20°), stirred solution of 0.5 g (3.4 mmol) of alcohol 4 in 10

ml of redistilled acetone the Jones reagent⁹ (2.7 M CrO₃ in H₂SO₄-H₂O) was added dropwise until an orange-brown coloration persisted. The acetone solution was then decanted from the chromium salts which were triturated with fresh acetone. The combined acetone solutions were concentrated under vacuum and the residue was taken up in 50 ml of ether. The organic layer was washed with two 20-ml portions of water and dried (MgSO₄). Evaporation of the ether and sublimation of the residue afforded 0.3 g (60%) of a waxy, white solid, mp 89–93°. Gc analysis of this material showed one compound with a retention time corresponding to that of the dihydro ketone 3. The infrared and nmr spectra of this material were identical with those of the authentic material.

Lithium Tri-*t*-butoxyaluminum Hydride Reduction of Dihydro Ketone 3.—A slurry of lithium tri-*t*-butoxyaluminum hydride was prepared by adding 2.3 g (31 mmol) of *t*-butyl alcohol to a solution of 0.38 g (10 mmol) of lithium aluminum hydride in 70 ml of dry ether. This mixture was stirred for 0.5 hr and 0.55 g (3.8 mmol) of ketone 3 in 5 ml of ether was added. The reaction mixture was stirred at ca. 25° for 5 hr and hydrolyzed by the addition of 10 ml of water, followed by 20 ml of 5 N hydrochloric acid. The ether layer was separated, washed with water, and dried (MgSO₄). Evaporation of the solvent and sublimation of the residue at 100° (0.5 mm) afforded 0.4 g (73%) of a white solid, mp 125–134°, mmp 128–134°, whose infrared spectrum was identical with that of the dihydro alcohol 4 described above. Analysis by gc showed only one product having a retention time identical with that of 4.

Registry No.—1, 5530-96-1; 2, 24708-29-0; 3, 22981-84-6; 4, 22981-83-5; 5, 24529-79-1; 6, 25296-31-5.

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Reaction of Cupric Alkoxide and Carbon Monoxide

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The reaction of cupric alkoxide with carbon monoxide was investigated. Cupric dimethoxide [Cu(OCH₃)₂], cupric dialkoxide of allyl alcohol [Cu(OC₂H₅)₂], cupric chloride methoxide [Cu(OCH₃)Cl], and cupric acetylacetonate methoxide [Cu(acac)(OCH₃)] were easily carbonylated to produce dialkyl carbonates. Carbonylation of cupric alkoxide in the presence of a secondary amine gave the corresponding carbamate. In the reaction, copper(II) was reduced to copper(I) and the extent of reduction was in good agreement with the yields of carbonylated products. The suggested reaction path involves the intermediate formation of carbomethoxycupric species by the insertion of carbon monoxide into the copper-oxygen bond of cupric alkoxide.

In our previous study,¹ the carbonylation of a ternary mixture of cupric acetate, methanol, and piperidine produced the corresponding carbamate. This finding suggested an intermediate carbomethoxycupric species which was formulated as being a product of the insertion of carbon monoxide into the copper-oxygen bond of cupric methoxide. In the present study, the reaction of cupric alkoxide with carbon monoxide was examined.

Studies of the carbonylation have hitherto been focused upon the insertion of carbon monoxide between carbon and metal of the groups VI to VIII. The carbonyl insertion into metal-oxygen and metal-nitrogen bonds has been little studied.² The present study

opens up a new field of carbonylation which involves copper(II) as the metal component and alkoxy group as the ligand component.

Carbonate Formation from Cupric Methoxide and Carbon Monoxide.—Cupric dimethoxide was readily carbonylated to produce dimethyl carbonate in high yields (Table I). Pyridine was a preferable reaction solvent, in which the carbonylation proceeded even at room temperature. Reactions in other solvents required higher reaction temperatures. Other cupric methoxide compounds such as Cu(OCH₃)Cl and Cu(acac)(OCH₃) were also effectively carbonylated to produce dimethyl carbonate. In the carbonylation of cupric dialkoxide of allyl alcohol, the olefinic group was not involved in the reaction and the product was diallyl carbonate. This finding provides an interesting contrast to the carbonylation of allyl alcohol in the presence of cobalt and rhodium carbonyl in which the olefinic

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