Metal Hydride Reductions of *endo*-Tricyclo[5,2,1,$0^{2,6}$]deca-4,8-dien-3-one (*endo*-Dicyclopentadienone)

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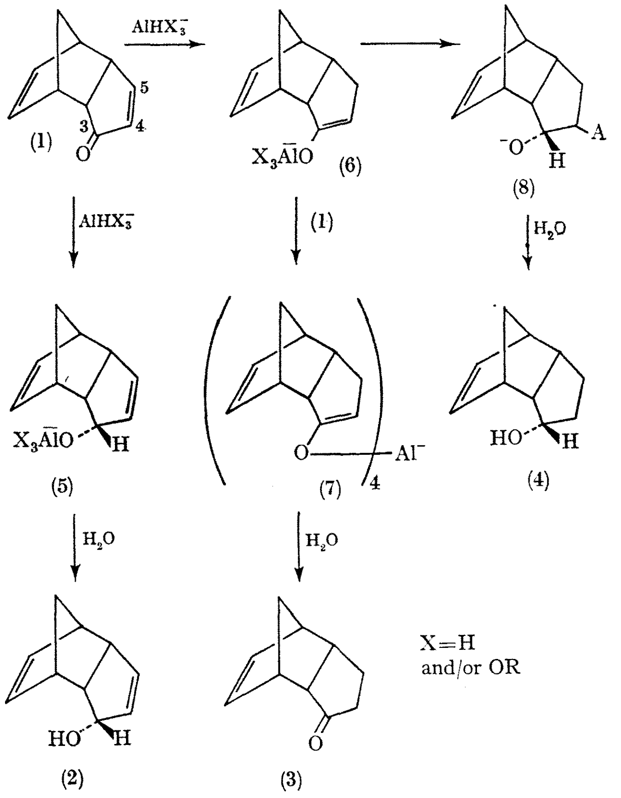
Summary Aluminium hydride, lithium tri-t-butoxyaluminium hydride, and sodium borohydride reduce specifically the carbonyl group, the double bond, and both the carbonyl group and the double bond, respectively, of a conjugated cyclopentenone, while lithium aluminium hydride gives all three products in varying amounts depending on the reaction conditions.

WE report several remarkably specific metal hydride reductions of the $\alpha\beta$-unsaturated ketone (1)[1] as well as some factors which influence the course of the lithium aluminium hydride reduction of (1). These results are probably applicable to other conjugated cyclopentenone derivatives.[2]

Reduction of the ketone (1) with aluminium hydride, lithium tri-t-butoxyaluminium hydride, and sodium borohydride gave either exclusively or mainly the allylic alcohol (2), the dihydro-ketone (3), and the dihydro-alcohol (4), respectively. Reduction of the ketone (1) with $LiAlH_4$ gave mainly carbonyl-reduced product (2) along with varying amounts of (3) and (4) depending on the reaction conditions. These results are summarized in the Table.

Woodward and Katz[1d] have reported previously the lithium aluminium hydride (0·060 M in ether) reduction of the ketone (1) to the allylic alcohol (2) in 71% yield. The structures of the ketone (3) (m.p. 100—103°) and dihydro-alcohol (4) (m.p. 134·5—137·5°) were determined by i.r. n.m.r., and high-resolution mass spectroscopy. Further structural evidence for (3) and (4) was provided by lithium tri-t-butoxyaluminium hydride reduction of the ketone (3) to (4) and re-conversion of the alcohol (4) into (3) by Jones oxidation.[5]

Tentative reaction paths to account for the results given in the Table are shown. Evidence consistent with formation of a carbon–aluminium bond in (8) was obtained by carrying out the reduction of (1) with lithium aluminium deuteride. Work-up with H_2O gave the alcohol (4) which contained two deuterium atoms per molecule, while work-up with D_2O led to incorporation of three deuterium atoms.† In both cases n.m.r. 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. Further discussion of the mechanism and full spectral data will be presented in the full publication.



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)	(3)	(4)
AlH_3 (3 $LiAlH_4$ + $AlCl_3$)[b] in Et_2O[c]	76	100	—[d]	—[d]
$Li(O\text{-}Bu^t)_3AlH$ ($LiAlH_4$ + 3 Bu^tOH)[e] in Et_2O[c]	70	1	83	16
$NaBH_4$ in MeOH[c]	72[f]	—[g]	—[g]	100
$LiAlH_4$ (0·017 M) in Et_2O[h] (normal addition)[c]	89	97	—[i]	3
$LiAlH_4$ (0·087 M) in Et_2O[h] (normal addition)[c]	94	65	17	18
$LiAlH_4$ (0·078 M) in Et_2O[h] (inverse addition)[j]	96	74	26	—[i]

[a] More than two equivalents of hydride per mole of ketone (1) were used in all experiments except that with 0·017 M-$LiAlH_4$ where one equivalent was used. Reactions carried out either at 0° or *ca.* 25° for 0·5—several hr. [b] Prepared according to procedure of Jorgenson.[3] [c] Ketone (1) added to hydride solution. [d] Less than 2% by g.l.c. analysis. [e] Prepared according to the procedure of Brown and McFarlin.[4] [f] The trialkylborate of (4) was also isolated in 8% yield. [g] Probably less than 5% formed. [h] The initial ketone (1) concentration was 0·067 M. [i] Less than 1% by g.l.c. analysis. [j] Hydride solution added dropwise over 1 hr. to ketone (1) solution.

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† The O-deuterium was washed out with H_2O.

[1] (a) H Hock and F. Depke, *Chem. Ber.*, 1951, **84**, 356; (b) K. Alder and F. H. Flock, *ibid.*, 1954, **87**, 1916; (c) M. Rosenblum, *J. Amer. Chem. Soc.*, 1957, **79**, 3179; (d) R. B. Woodward and T. J. Katz, *Tetrahedron*, 1959, **5**, 70.

[2] H. C. Brown and H. M. Hess have observed similar results for the hydride reductions of cyclopent-2-enone and *endo*-tricyclo[5,2,1,$0^{2,6}$]-dec-4-en-3-one; private communication.

[3] M. J. Jorgenson, *Tetrahedron Letters*, 1962, 559.

[4] H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, 1958, **80**, 5372.

[5] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lenin, *J. Chem. Soc.*, 1953, 2548.