Selective Reduction of 2-Ene-1,4-diones and 2-En-1-ones with Di-i-butylaluminium Hydride

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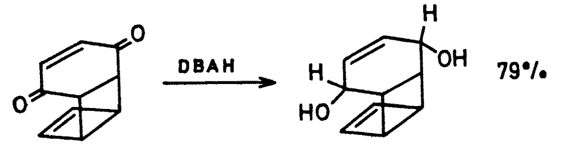
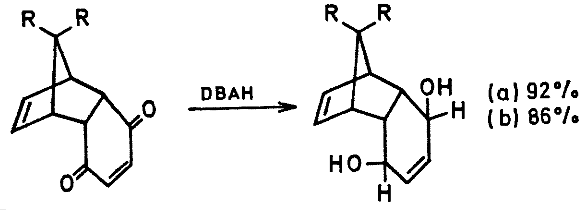
Summary Reduction of 2-ene-1,4-diones and 2-enones with di-i-butylaluminium hydride provides the corresponding unsaturated alcohols in excellent yields and this reagent appears to be superior to other metal hydrides including aluminium hydride.

REPORTED attempts to reduce 2-ene-1,4-diones and 2-en-1-ones (*e.g.* cyclopentenones) selectively to the corresponding unsaturated alcohols have frequently met with only marginal success, the desired product, if present at all, being accompanied by large amounts of substances arising from the saturation of the olefinic bond. We have used di-i-butylaluminium hydride DBAH[1] for such reactions and report its high selectivity.

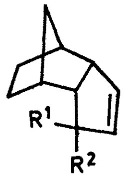
Treatment of compound (**1**)[2] with $NaBH_4$, $LiAlH_4$, $Li(OBu^t)_3AlH$, $Al(OPr^i)_3$–propan-2-ol, and AlH_3 invariably[3] afforded a complex mixture and failed to provide the desired unsaturated hydroxy-compound (**2**) even after extensive chromatography. In contrast, selective reduction proceeded smoothly with DBAH in benzene and (**2**) (m.p. 135—137°) was isolated in 79% yield. Similarly, (**3a**) and (**3b**)† were converted by this reagent into the corresponding alcohols (**4a**) and (**4b**) in 92 and 86% yield, respectively.



(1) **(2)**



(3) a; R = H
b; R = OEt **(4)**



(**5a**) $R^1,R^2 = O$
(**5b**) $R^1 = OH, R^2 = H$
(**5c**) = (**5a**) with the double bond reduced
(**5d**) = (**5b**) with the double bond reduced

In order to compare the selectivity of DBAH with that of AlH_3, we have reduced (**5a**) and cyclopent-2-enone (**6**) with DBAH. Aluminium hydride was recently recommended for the reduction of cyclopentenones to cyclopentenols.[4] Each reaction was performed at 0—5° under nitrogen by the slow addition of a benzene solution of 1·5 mole equiv. of DBAH to 1·0 mole equiv. of enone in benzene. After two hours additional stirring, the aluminium salts were decomposed at 5° with a large excess of methanol. The precipitated Al salt was removed by filtration and washed several times with hot methanol. The combined filtrate and washings was stripped of solvent and the product distilled. The g.l.c. analysis of the product composition and purity was carried out using naphthalene as an internal standard. The results (Tables 1 and 2) demonstrate that DBAH leads to the higher yields and cleaner reductions. Di-isobutylaluminium hydride is therefore an exceptionally attractive reagent for organic synthesis.

TABLE 1

Reductions of (**5**)

Reagent	Isolated % yield of allylic alcohol	% Composition[a,b] (**5a**)	(**5b**)	(**5c**)	(**5d**)
AlH_3[c]	65	0·1	86	10	4·0
DBAH	90	1·0	98	0·0	0·8

[a] The composition of the product was determined using an 18 ft. Silicone Gum Rubber UCW-98, 10%, 80—100 WAWDMCS column.

[b] The absence of the saturated ketone in the reduction mixture was established by co-injection experiments using a 6 ft. Reoplex 10% WAWDMCS column.

[c] Data for the AlH_3 reduction were taken from ref. 4a.

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TABLE 2

Reductions of (**6**)

Reagent	Isolated % yield of allylic alcohol	(**6**)	% Composition[a,b] Cyclopenten-2-ol	Cyclopentanone	Cyclopentanol
AlH_3[c]	79	0·0	90·0	6·1	3·9
DBAH	83	0·5	99·0	0·0	0·5

[a] The composition of the product was determined using a 6 ft. Carbowax 10% 20M 80—100 WAWDMCS column.

[b] Some isobutanol was liberated from isobutoxide contaminants in the reagent DBAH.

[c] Data for the AlH_3 reduction were taken from ref. 4a.

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† Performed by Dr. P. M. Baker of this laboratory.

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[4] (a) H. C. Brown and H. M. Hess, *J. Org. Chem.*, 1969, **34**, 2206; (b) W. L. Dilling and R. A. Plepys, *Chem. Comm.*, 1969, 417.