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METAL-ASSISTED REACTIONS—12[1]

UNUSUAL SELECTIVITY IN THE REDUCTION OF KETONES WITH ZINC OR CADMIUM *BIS*-TETRAHYDROBORATE/DIMETHYLFORMAMIDE COMPLEX

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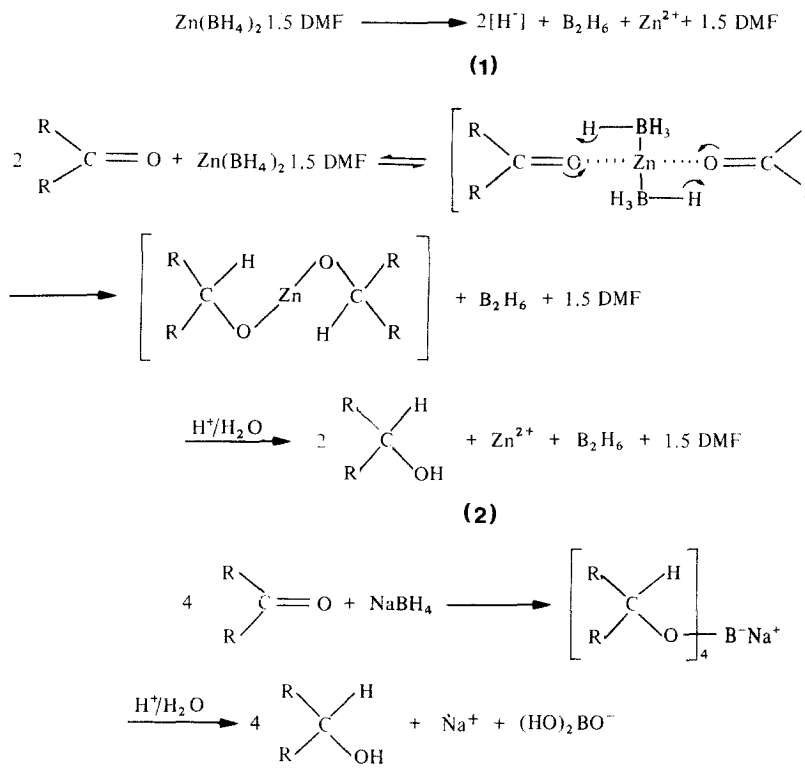
Abstract—Zinc *bis*-tetrahydroborate forms a solid complex with dimethylformamide (DMF) of composition, $Zn(BH_4)_2$ 1.5DMF. Unlike zinc *bis*-tetrahydroborate itself, the complex with DMF can be stored as a solid at room temperature. Ketones and aldehydes are reduced to the corresponding alcohols by the complex but the mechanism of reduction appears to be different from that using zinc *bis*-tetrahydroborate itself and from other tetrahydroborates in that only one hydride equivalent from each BH_4^- unit is utilized and not four. Further, although saturated aliphatic ketones are reduced rapidly to alcohols, aromatic ketones react much more slowly and α,β-unsaturated ketones react very slowly so that the complex appears to have selective reducing potential with regard to different classes of ketones. It is also apparent that the zinc *bis*-tetrahydroborate/DMF complex reduces sterically hindered saturated ketones much more slowly than it does unhindered ketones. An analogous cadmium *bis*-tetrahydroborate/DMF complex can be prepared in solution and reacts with ketones similarly to the zinc complex.

Although zinc *bis*-tetrahydroborate is known,[2] it has been little used as a reagent for the reduction of organic compounds, probably because of the readier availability of other versatile and thermally more stable hydride donors such as sodium tetrahydroborate and lithium tetrahydroaluminate. The poor thermal stability of zinc *bis*-tetrahydroborate makes it unavailable commercially. However, as a hydride donor, zinc *bis*-tetrahydroborate is less basic than sodium tetrahydroborate and is particularly suitable for reduction of alkali-sensitive compounds. Zinc *bis*-tetrahydroborate has been preferred to other hydride donors in several syntheses,[3] including some leading to prostaglandins,[4] and its action on various types of CO groups has been investigated.[5] These last experiments suggest that the reagent has little selectivity since all types of ketones, aldehydes, acyl halides and carboxylic acids are reduced rapidly to the corresponding alcohols; primary amides and oximes are reduced slowly to amines. Zinc *bis*-tetrahydroborate exhibits some stereoselectivity as demonstrated by its reduction of a β-keto ester to a mixture (99:1) of the erythro- and threo-isomers.[6]

Our interest in zinc *bis*-tetrahydroborate was aroused with the discovery that it forms a stable, solid complex with DMF, $Zn(BH_4)_2$1.5DMF.[7] This complex showed no appreciable deterioration on storage for over one year at room temperature under anhydrous conditions. Similar complexes are known, as for example the complex with trimethylamine, $Zn(BH_4)_2 2NMe_3$, but there appear to have been no investigations of their reducing properties, it being generally supposed that these would be the same as those of zinc *bis*-tetrahydroborate itself. As the complex with DMF was so easy to make, store and handle, it was decided to investigate the reducing capacity of the complex towards simple CO functional groups.

With benzaldehyde and cyclohexanone, reduction of the CO group to the fully reduced alcohol was complete in 10 min at room temperature, using an excess of the zinc *bis*-tetrahydroborate/DMF complex. Further experiments with cyclohexanone showed that not all of the hydrogen of the tetrahydroborate was active as hydride. Although there are nominally eight hydride equivalents per molecule of the complex, it was found that a molar ratio of cyclohexanone to tetrahydroborate complex of 4:1 resulted in much of the ketone remaining unreduced even after 16 hr. Similar reactions with different molar ratios of complex and cyclohexanone indicated that, stoichiometrically, the reaction required one mole proportion of the *bis*-tetrahydroborate to two of cyclohexanone for complete reduction. These results suggested that the remaining hydrogens were being released with the boron as diborane, as shown in eqn (1). To examine this possibility, a mixture of cyclohexanone and cyclopentene in equimolar proportions was reacted with a half-molar proportion of zinc *bis*-tetrahydroborate/DMF complex. According to eqn (1), these proportions should ensure complete reduction of the cyclohexanone to cyclohexanol and conversion of the cyclopentene into its adduct with diborane. The reaction mixture was worked up oxidatively to convert any cyclopentyldihydroboron into cyclopentanol. After 10 min reaction, gas chromatography showed that all the cyclohexanone had been reduced to cyclohexanol and all the cyclopentene converted into the diborane adduct (isolated as cyclopentanol). From these results, we suggest that zinc *bis*-tetrahydroborate/DMF complex reacts with ketones along the lines indicated in eqn (2). For comparison, the generally accepted[9] mode of action of sodium tetrahydroborate with ketones is illustrated in eqn (3).



(1)

(2)

(3)

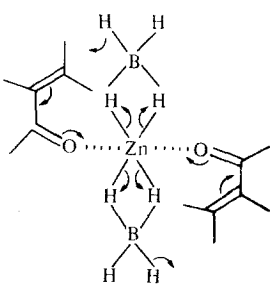
$ZnCl_2$ co-ordinates effectively with the CO function of acetophenone[10] and it is proposed in eqn (2) that bonding to Zn by the CO oxygen atom before and after reduction, prevents the formation of the oxyborate with other CO groups as shown in eqn (3) and therefore allows the release of BH_3 (or B_2H_6). Under these circumstances, the B_2H_6 is available for addition[11] to a double bond as in the test experiments with cyclopentene described above. Initial co-ordination of ketone to the zinc *bis*-tetrahydroborate complex is shown in reaction (2) as reversible. Zn^{2+} has been described as a borderline soft Lewis acid which, on the hard and soft acid/base principle,[12] is presumably softer (see below) when co-ordinated to a group such as DMF which can reduce the central positive charge by spreading it over a larger volume, as indicated in the Scheme (4).

(4)

In reaction sequence (3), the tetrahydroborate ion (soft base[13]) attacks the C atom of the CO group (soft acid) to release BH_3 (soft acid[14]) which then bonds to the CO oxygen atom.[15] In the presence of added base (e.g. pyridine), the released BH_3 (or B_2H_6) bonds preferentially to the pyridine and therefore each tetrahydroborate ion provides only one hydride equivalent.[16,17] In reaction sequence (2) it is supposed that the O atom of the CO group that is already co-ordinated to the Zn centre, simply forms a stronger bond to the Zn ion after the hydride ion has been transferred and allows the release of BH_3 (or B_2H_6). This difference in reaction modes is important in considering the selectivity of the zinc *bis*-tetrahydroborate complex towards different types of ketones (see below).

Reaction of the zinc *bis*-tetrahydroborate/DMF complex with sterically unhindered saturated ketones was generally rapid. For example, 2-indanone (Table 1) was reduced to the corresponding alcohol by the complex in 15 min at room temperature. In contrast, reaction of the complex with aromatic ketones was much slower. Benzophenone and 1-tetralone (Table 1) required 10–16 hr for reduction to the corresponding alcohols and needed an excess of the complex for complete reduction. Excess of tetrahydroborate was required possibly because of its slow decomposition in solution over these extended periods of time.

Although aromatic ketones were slow to react with the zinc *bis*-tetrahydroborate/DMF complex, α,β-unsaturated ketones reacted even slower. With isophorone (3,5,5-trimethylcyclohex-2-enone), no reduction was



(5)

Table 1. Reduction of ketones with zinc *bis*-tetrahydroborate/DMF complex (Z) or with cadmium *bis*-tetrahydroborate/DMF reagent (C)

Ketone	Reagent	Reaction Time[a]	Reduced Product	Yield %	Recovery of Starting Material (%)
Cyclohexanone	Z	10 min	Cyclohexanol	100	0
	C	25 min(-35°)		100	0
Cyclohexenone	Z	5 hr	-	0	100
	C	1 hr(-35 to 20°)			
2-Indanone	Z	15 min	2-indanol	100	0
Benzophenone	Z	16 hr	benzhydrol	100	0
1-Tetralone	Z	10 hr	1-tetralol	100	0
3,5,5-Trimethyl-cyclohexenone	Z	26 hr	-	0	100
1,3-Diphenylpropen-one	Z	16 hr	1,3-diphenylpropen-1-ol	60	25
			1,3-diphenylpropan-1-ol	15	
3-Penten-2-one	C	2 hr	-	0	96
		24 hr	3-penten-2-ol	92	0[b]
1-Phenyl-1,3-hexadien-5-one	C	1 hr	-	0	100
		24 hr	1-phenylhexa-1,3-dien-5-ol	98	0[b]
9-Methyl-$\Delta^{5(10)}$-octalin-1,6-dione	Z	1 hr	9-Methyl-$\Delta^{5(10)}$-octalin-1-ol-6-one	100	-
4-Androsten-3,17-dione[c]	Z	9.5 hr	4-androsten-3,17-diol	30	0
			4-androsten-3-ol-17-one	20	
			testosterone	40	
Progesterone[c]	Z	26 hr	4-pregnen-3-ol-20-one	20	0
			4-pregnen-3-one-20-ol	25	
			4-pregnen-3,20-diol	55	

a. These are typical reaction times at room temperature (ca. 18-20°). Reactions carried out at different temperatures are indicated by the temperature given in parentheses.

b. No product of saturation of the double bond was identified.

c. These reactions were very slow, and a large excess of the complex(Z) was used to react all the starting material in a reasonable time. Under these forcing conditions, considerable over-reduction occurred. With the normal stoichiometric amounts of complex(Z), selective reduction of the saturated ketone occurred, but slowly, and considerable quantities of starting material were recovered in the reaction times usually used for saturated ketones (10-15 min). See text for further details.

observed over a period of 26 hr, even with an excess of the reagent. Similarly, the structurally simpler and less sterically hindered enone, cyclohexenone, afforded only starting material after 5 hr with the tetrahydroborate complex.

The above results suggested that compounds should be examined in which two types or "mixed" types of ketone were present. Benzalacetophenone (1,3-diphenylpropenone), both an aromatic and an α,β-unsaturated ketone, reacted slowly with the tetrahydroborate complex at room temperature to give, after 16 hr, a 60% yield of the alcohol, 1,3-diphenylprop-2-en-1-ol, together with 25% of starting material and 15% of 1,3-diphenylpropan-1-ol, indicating that some reduction of the double bond had occurred. 9-Methyl-$\Delta^{5(10)}$-octalin-1,6-dione, containing two ketone functions, one saturated and one unsaturated, reacted with zinc *bis*-tetrahydroborate/DMF complex in 1 hr at room temperature to yield 70% of 9-methyl-$\Delta^{5(10)}$-octalin-1-ol-6-one (reduction of the saturated ketone function) and 30% of starting material. By use of an excess of reducing agent, reduction to the octalin-1-ol-6-one occurred within 15 min. With 4-

androsten-3,17-dione, a large excess of the tetrahydroborate complex was required to cause all of the starting material to react in 9.5 hr but, under these forcing conditions, only a 40% yield of the required keto - alcohol, 4 - androsten - 3 - one - 17 - ol, was isolated together with 20% of 4 - androsten - 3 - ol - 17 - one and 4 - androsten - 3,7 - diol (30%). This result, similar to the result of reducing androstane - 3,17 - dione with sodium borohydride where reduction of the 17-keto group was incomplete,[18] suggests that approach of the zinc *bis*-tetrahydroborate/DMF complex to the 17-keto function in the 5-membered steroidal D-ring is sterically hindered, leading to slow reduction.[16] To reduce the 17-keto group in a reasonably short time, a large excess of the reducing agent had to be used and resulted in some reduction of the α,β-unsaturated ketone system. Similarly, progesterone, having an α,β-unsaturated ketone function in the A-ring and a saturated (C-20) ketonic side-chain, required a three-fold excess of zinc *bis*-tetrahydroborate/DMF complex and 26 hr to effect reaction of all starting material. Under these conditions, only a 25% yield of 4-pregnen-3-one-20-ol was obtained, along with 20% of 4-pregnen-3-ol-20-one and 55% of 4-pregnen-3,20-diol. As cyclopentanone reacts readily with the tetrahydroborate complex, these results indicate that steric crowding around the 17- or 20-keto groups in steroids is sufficient to slow the reaction of the bulky tetrahydroborate complex with the saturated ketone and allows competitive reduction of the α,β-unsaturated ketone to occur. If reaction times typical for saturated ketones (10–15 min) were used, selective reduction occurred but considerable amounts of starting material were recovered; even after 1–2 hr, reaction of the saturated ketone in the steroids with the reducing agent was very limited. It was notable in these cases that no evidence for 1,4-addition of hydride to the α,β-unsaturated system was observed.[13,16]

The differentiation of the zinc *bis*-tetrahydroborate complex between saturated and unsaturated ketone functions is remarkable in view of the rapidity with which tetrahydroborates generally reduce these functional groups. There is some differentiation by sodium tetrahydroborate between saturated and α,β-unsaturated ketones. For example, in isopropanol, Δ^4-cholest-3-enone is reduced some seven times slower than is cholestan-3-one.[19] Usually, an increase in reducing power accompanies the addition of metal ions such as Mg^{2+} and Sr^{2+} to solutions of sodium tetrahydroborate.[20]

As remarked above, the reactivity of carbonyl groups towards hydride reducing agents[11] has been discussed in terms of the hard and soft acid/base principle. Although the C atom of the CO group in acids, esters and amides is considered to be a hard acceptor of electrons, the opposite is found for ketones and aldehydes in which this C atom is soft. Further, both the CO carbon and O atom become harder with conjugation to an unsaturated system. These electronic effects can be related also to class *a* and class *b* behaviour of donors and acceptors.[21] In the α,β-unsaturated ketones, the C atom becomes softer than the CO carbon and either 1,2- or 1,4-addition of hydride can occur depending on the softness or type of hydride reagent used. For example, sodium trimethoxyhydroborate causes mainly 1,2-reduction of cholestenone to cholestenol but sodium tetrahydroborate effects 1,4-reduction to cholestanol.[16] Although Zn^{2+} itself has been described as a borderline soft acid,[22] it is likely that co-ordination of DMF spreads the positive charge (Scheme 4), making the Zn much softer. For example, using Klopman's method[23] for estimating the ordering of softness of cations, Zn^{2+} changes from being a borderline soft acid to being as soft as Ag^+. Because the tetrahydroborate ion is a soft donor, the degree of covalency of the binding of BH_4^- to Zn^{2+} complexed with DMF will increase from its value for BH_4^- with uncomplexed Zn^{2+}. Not only does this help to stabilize the zinc *bis*-tetrahydroborate but it also makes the hydride softer. The increased soft character of the zinc *bis*-tetrahydroborate/DMF complex means that the binding of the CO oxygen atom (hard donor, eqn 2) will be less energetically favoured, particularly for conjugated enones. At the same time, the transfer of hydride ion from the soft tetrahydroborate to the CO carbon atom also becomes energetically less favourable. These two effects, acting in concert, can explain the order of ease of reduction found experimentally, i.e. saturated ketone ≈ aromatic aldehyde > aromatic ketone > α,β-unsaturated ketone. However, it is still not clear why addition of hydride ion to the soft γ-C atom of the enone system appears to be disfavoured. It is possible that, if the conjugated ketones cannot bind effectively to the Zn and the tetrahydroborate entity is strongly bound covalently to the large Zn^{2+}/DMF centre, then approach of the γ-C to the tetrahydroborate is for statistical and topological reasons a relatively rare event. Even if the α,β-unsaturated ketone binds to the Zn complex, any transfer of hydride from covalently bound BH_4^- would require an unfavourable quasi 8-membered ring transition state (Scheme 5).

Zn and Cd are close in the periodic table of elements and their compounds have many similar properties. A cadmium *bis*-tetrahydroborate/DMF reagent appears to be less active than the Zn compound because it has been shown to be effective for the rapid reduction of acid chlorides to aldehydes, without significant over-reduction to the corresponding alcohol.[7] Like the zinc *bis*-tetrahydroborate/DMF reduction of ketones, only one hydride equivalent of the BH_4^- entity is effective in this reduction of acid chlorides. Confirmation of the stronger reducing power of zinc *bis*-tetrahydroborate/DMF over cadmium *bis*-tetrahydroborate/DMF was evident in attempts to reduce benzoyl chloride to benzaldehyde using the Zn reagent. Whereas the Cd reagent gives an 80% yield of benzaldehyde,[7] the Zn reagent under similar conditions gave only 20%, the remainder of the reduction product being benzyl alcohol.

Because of the gentler reducing action of cadmium *bis*-tetrahydroborate/DMF with acid chlorides its use for reduction of ketones was investigated. As with its Zn counterpart, reduction of saturated ketones to alcohols occurred within 10–15 min but reduction of enones and dienones was much slower, frequently requiring many hours to effect complete reduction to the corresponding alcohol. Thus, stirring 3-penten-2-one or 1-phenylhexa-1,3-dien-5-one with the Cd reagent for 1–2 hr at room temperature yielded only starting material and no reduction products (Table 1). On leaving the mixture to stand for 24 hr at room temperature, none of the starting material remained and only products of the reduction of the ketone to alcohol were isolated. No products of reduction of the double bond were observed.

The Cd reagent (prepared *in situ*) and the zinc *bis*-tetrahydroborate appear to react similarly in their reducing action on saturated ketones and enones, although there must be rate differences. As the Zn complex is easy to prepare and stable at room temperature, it is preferred

over the corresponding Cd compound for selective reduction of ketones but not for reduction of acid chlorides.

EXPERIMENTAL

All products of reduction are known compounds and were identified by comparison with authentic materials in their chromatographic (GC, TLC) and spectroscopic (^{1}H-NMR, IR) properties. Yields are based on peak areas from gas chromatographic results using internal standards or from integrals of peak areas of characteristic proton resonances in ^{1}H-NMR spectra.

Preparation of $Zn(BH_4)_2$1.5DMF. An ethereal soln of zinc *bis*-tetrahydroborate was prepared from $ZnCl_2$ and finely-ground sodium tetrahydroborate.[2] To this stirred soln (200 ml; 27 mmole) at −5° was added dropwise dry DMF (3.8 g; 50.6 mmole). A white ppt of the *bis*-tetrahydroborate/DMF complex was formed. Solvent was decanted from the ppt which was washed by decantation with fresh diethyl ether (2 × 15 ml). Residual solvent was removed by drying the complex in a stream of argon or in a vacuum desiccator (drying of the complex by suction of moist air through it in a filter funnel led to a product depleted in hydride ion equivalents (active hydrogen) and occasionally resulted in the complex inflaming). The dry reagent, $Zn(BH_4)_2$1.5 DMF,[28] was stored in a well-stoppered vessel at 0° although other specimens, stored for periods of more than a year at room temp (*ca* 18–20°), appeared to have lost none of their activity by storage at the higher temperature.

Preparation of cadmium bis-*tetrahydroborate*/DMF. This reagent has not been isolated as such but has been prepared in soln.[7] To a stirred suspension of $CdCl_2$ 1.5DMF (5.5 g; 25 mmole) in dry acetonitrile (25 ml) at 0° was added dropwise a soln of $NaBH_4$ (0.76 g; 20 mmole) in a mixture of dry DMF (5 ml) and acetonitrile (40 ml) over a period of 10 min. The mixture was stirred for a further 10 min at 0° and then used as in the experiments described below.

Typical reduction of a saturated ketone with zinc bis-*tetrahydroborate*/DMF *complex.* 2-Indanone (527 mg; 4.0 mmole) was added to a stirred suspension of $Zn(BH_4)_2$1.5DMF (414 mg; 2.0 mmole) in dry acetonitrile (12 ml) at room temp (*ca* 18°). After 15 min, water (5 ml) followed by excess of dil HCl was added and the mixture was extracted with diethyl ether to give 2-indanol (391 mg; 73% yield of pure material; needles, m.p. 68–69°, lit. 70°;[29] further characterized through its ^{1}H-NMR and mass spectra).

Typical reaction of an enone with zinc bis-*tetrahydroborate*/DMF *complex.* To a stirred suspension of zinc *bis*-tetrahydroborate/DMF (250 mg; 1.22 mmole) in dry acetonitrile (10 ml) at room temp was added 3,5,5-trimethylcyclohexenone (isophorone; 169 mg; 1.22 mmole). After 2 hr, addition of excess of dil HCl followed by extraction with ether gave a 90% recovery of starting material with no indication of any reduction having occurred. In a separate experiment, the mixture was left for 26 hr before being worked up and, again, only starting material was recovered.

Reduction of cyclohexanone with zinc bis-*tetrahydroborate*/DMF *complex in the presence of cyclopentene.* A mixture of cyclohexanone (251 mg; 2.56 mmole) and cyclopentene (176 mg; 2.58 mmole) was added to a stirred suspension of zinc *bis*-tetrahydroborate/DMF (255 mg; 1.25 mmole) in dry acetonitrile (7 ml) at room temp. After 10 min, an aliquot was treated with water and 30% H_2O_2[30] and extracted with ether. Gas chromatography (10% Reoplex at 105°) showed that complete reduction of the cyclohexanone to cyclohexanol had occurred and that the cyclopentene had been converted completely into cyclopentanol.

Reduction of an aromatic ketone with zinc bis-*tetrahydroborate*/DMF *complex.* 1-Tetralone (287 mg; 1.96 mmole) was added to a stirred suspension of zinc *bis*-tetrahydroborate/DMF (205 mg; 1.0 mmole) in dry acetonitrile (7 ml) at room temp. After 10 hr, GC and ^{1}H-NMR spectroscopy showed that complete reduction to 1-tetralol had occurred.

Typical reduction of a saturated ketone with cadmium bis-*tetrahydroborate*/DMF *reagent.* To the Cd reagent in acetonitrile (prepared as described above; 25 mmole) was added dropwise a soln of cyclohexanone (1.96 g; 20 mmole) in acetonitrile at −35° over a period of 15 min. After a further 10 min at −35°, the mixture was worked up by addition of excess of dil HCl and extraction with diethyl ether to give a 100% yield of cyclohexanol.

Typical reduction of an enone with cadmium bis-*tetrahydroborate*/DMF *reagent.* To the Cd reagent in acetonitrile (prepared as above; 25 mmole) was added a soln of 3-penten-2-one (1.64 g; 20 mmole) in acetonitrile (25 ml) at −35° over a period of 15 min. After 15 min at −35°, GC showed only starting material and after 1 hr at room temp, again only starting material. On leaving the soln to stand at room temp for 24 hr, reduction to 3-penten-2-ol had occurred to the extent of about 92%, as shown by GC.

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