Metal-assisted Reactions. Part 8.[1] Selectivity in the Reaction of Organic Halides with Tetrahydroborate and the Reduction of Acyl Halides to Aldehydes

By Ian D. Entwistle and Peter Boehm, Shell Biosciences Laboratory, Shell Research Ltd., Sittingbourne, Kent ME9 8AG

Robert A. W. Johnstone,* and Robert P. Telford, The Robert Robinson Laboratories, The University, Liverpool L69 3BX

Addition of metal ions such as Cu^+, Cu^{2+}, Cd^{2+}, and Zn^{2+} with dimethylformamide to sodium tetrahydroborate in acetonitrile affords a reducing medium in which acyl halides are converted to aldehydes but alkyl, aryl, and benzylic halides are unaffected. The inertness of these last, synthetically useful, functional groups along with the inertness of other potentially reducible groups, makes the reagent very selective for direct reduction of acyl halides to aldehydes. The reducing solution is stable, readily prepared from cheap materials, rapid in action, and easy to use, making the conversion of acids to aldehydes *via* acyl halides a routine synthetic procedure.

SODIUM TETRAHYDROBORATE is a widely-used reductant with many applications in organic synthesis, with cheapness and ease of handling being amongst its attractive features. The reactivity of sodium tetrahydroborate has been enhanced by replacing up to three hydrogens with alkoxy groups, the resulting alkoxyhydroborates resembling lithium tetrahydroaluminate in effectiveness for reduction.[2] Alternatively, tetrahydroborate reducing activity is enhanced [2] by addition of metallic ions such as Li^+, Mg^{2+}, and Al^{3+}. Whereas sodium tetrahydroborate will not reduce esters under normal conditions, it does so in the presence of lithium or magnesium chloride. Zinc tetrahydroborate can be used to reduce compounds sensitive to the base present as a stabilizer in sodium tetrahydroborate.[3] Use of Pd, Pt, Os, Ir, Cu, Ni, and Co salts with tetrahydroborate has been advocated for the reduction of nitro, nitroso, cyano, and amide groups to amino. In these cases, the metallic ions are reduced to a finely-divided metallic state effective, along with the hydrogen produced, for the reduction;[4a] similarly, palladised charcoal and sodium tetrahydroborate have been employed.[4a] Use of sodium tetrahydroborate has been described for dehalogenation with palladised charcoal [5] and formation of azoxy-compounds with cobaltous salts.[6] The activity of hydroborates is strongly influenced by solvents.[7] Further, metal hydroborates may be made separately and used as such but often reducing solutions are prepared in which the metal hydroborate is nominally prepared by metathetical reaction and used without isolation of the hydroborate species. In these latter cases, the structure of the reducing species may well be unknown and could range from that of a simple, ionic hydroborate to that of a complex, covalent salt. In the present work, the interplay of metal ions and solvent was found to be effective in the action of a reducing solution prepared by metathesis. Initial experiments were undertaken to develop an alternative to direct methods of reducing acyl chlorides to aldehydes, as for example those in refs. 8 and 9.

RESULTS AND DISCUSSION

When mixed in 1 : 2 molar proportions at −10 °C, solutions of copper(II) chloride and sodium tetrahydro-borate in dimethylformamide afforded a brown solution which slowly effervesced. Addition of benzoyl chloride to this solution followed by work-up two or three minutes later gave a 46% yield of benzaldehyde. In an attempt to stabilize the solution, co-ordinating ligands such as triethylamine, triethyl phosphite, and triphenylphosphine were added, and these slightly improved the yield of aldehyde. As the copper(II) salt was obviously (from colour changes) being reduced to copper(I), and as copper(I) tetrahydroborate was known [10] (its reactions with organic functional groups had not been investigated), a reducing solution was prepared from a 1 : 1 molar ratio of copper(I) chloride and sodium tetrahydro-borate in dimethylformamide at −5 to −10 °C. Reaction with benzoyl chloride gave 63% of benzaldehyde together with some benzyl alcohol and benzoic anhydride. The benzoyl chloride and ' copper tetrahydroborate ' were mixed in a 1 : 1 molar ratio and, with the excess of hydride, it is surprising that any aldehyde remained unreduced to benzyl alcohol. Vigorous conditions were required to reduce aromatic acid chlorides to alcohols with sodium tetrahydroborate in dioxan,[11] and we concluded that solvent was important in this reaction. When the above reduction with copper(I) salt was attempted in acetonitrile, all the benzoyl chloride was recovered. Benzaldehyde was obtained only when solvents such as dimethylformamide, dimethylacetamide, and hexamethylphosphoramide were present, alone or admixed with other solvents, and this suggested that an acyl halide–solvent complex was being reduced, not the acyl halide alone. Such complexes are well known and have been postulated as intermediates in other reactions.[12] Addition of ' inert ', aprotic solvents like diethyl ether and carbon tetrachloride to dimethylformamide did not greatly affect reaction yields but acetonitrile was found best for all-round solubility of inorganic and organic compounds; small additions of diglyme or hexamethylphosphoramide were useful in preparation of the reagents to solubilize the sodium tetrahydroborate.

The ' copper(I) tetrahydroborate ' solutions were unstable and consideration of the Periodic Table and known stabilities of other metal hydroborates [10,13] suggested that zinc(II) or cadmium(II) salts might be more useful.

Aldehydes (RCHO) produced by reduction of acid chlorides (RCOCl) with cadmium-moderated borohydride

R	Yield [a] (%)	M.p. (°C) (solvent) [a]	Lit. m.p. (°C) or analysis [b]
Ph	76, 80 [c]	241—242 (AcOH)	237 [28]
4-MeC$_6$H$_4$	89	238—240	233—234 [29]
4-ClC$_6$H$_4$	74	272 (EtOH)	270—271 [30]
4-NO$_2$C$_6$H$_4$	71	317—318 (xylene)	320 [31]
4-MeOC$_6$H$_4$	63	251—252 (AcOH)	253—254 [28]
4-NCC$_6$H$_4$	67	307—308 (AcOH)	295—298 [9]
2-MeC$_6$H$_4$	60	190—192	190—193 [29]
2-BrC$_6$H$_4$	62	199—200 (xylene)	203 [31]
2-MeO$_2$CC$_6$H$_4$	52	242—243 (xylene)	C, 52.3 (52.4); H, 3.6 (3.5); N, 16.0 (16.3)%
3-PhOC$_6$H$_4$	81	185—187 (toluene)	C, 60.7 (60.3); H, 3.6 (3.7); N, 14.9 (14.8)%
3,4,5-(MeO)$_3$C$_6$H$_2$	46	246—247 (AcOH)	246 [32]
4-ClC$_6$H$_4$CH(CHMe$_2$)	61	162—163 (MeOH)	C, 54.4 (54.2); H, 4.5 (4.5); N, 14.6 (14.9)%
PhCH$_2$	58	115—117 (EtOH–C$_6$H$_6$)	125—126 [33]
trans-PhCH=CH	71	253—254	253 [28]
n-C$_7$H$_{15}$	56	103 (EtOH)	106 [28]
Me$_3$C	32	209—210 (EtOH–AcOEt)	210 [34]
cyclo-C$_6$H$_{11}$	24	165—166 (MeOH)	172 [35]
cyclo-C$_3$H$_5$	62	188—189 (MeOH)	184—185 [36]
cis-2-EtO$_2$C-cyclo-C$_3$H$_4$	50	158—159 (MeOH)	C, 48.5 (48.5); H, 4.3 (4.4); N, 17.4 (17.4)%
cis-2-EtO$_2$C-3,3-Me$_2$-cyclo-C$_3$H$_2$	74	127—129 (MeOH)	C, 44.1 (45.0); H, 3.3 (3.7); N, 14.8 (15.0)%
trans-MeCH=CH	54	182—184 (EtOH–AcOEt)	184—185 [37]
n-C$_{12}$H$_{25}$Cl [d]			
n-C$_{12}$H$_{25}$Br [d]			
n-C$_{12}$H$_{25}$I [d]			
C$_5$H$_5$CH$_2$Cl [d]			

[a] As 2,4-dinitrophenylhydrazone (recrystallized from stated solvent). ^{1}H N.m.r. spectra consistently indicated yields of the aldehyde ca. 10% greater than the isolated yields of recrystallized 2,4-dinitrophenylhydrazone. [b] All are 2,4-dinitrophenylhydrazones. For previously unknown 2,4-dinitrophenylhydrazones, required percentages for C,H,N are given in parentheses after the values found by elemental analysis. [c] Yields obtained in different laboratories using same conditions. [d] Actual compound used and recovered in 100% yield with no evidence (^{1}H n.m.r.) for displacement of halogen by hydrogen.

A solution of cadmium(II) chloride and sodium tetrahydroborate (1 : 2 molar ratio) in dimethylformamide reduced benzoyl chloride to benzaldehyde in 60—70% yield at −10 °C. Conveniently, the cadmium chloride was dried by crystallization from dimethylformamide to give CdCl$_2$·1.5DMF.[14] This amount of dimethylformamide was sufficient for reduction and use of CdCl$_2$·1.5DMF in acetonitrile gave a 76% yield of benzaldehyde. The other acyl halides in the Table were reduced similarly.

As the examples in the Table show, reduction of acyl chloride to aldehyde can be effected rapidly in good yield, in the presence of other reducible substituents such as nitrile, nitro, ester, and alkene. The range of compounds studied is much wider than previously reported.[15] Some notably selective reductions are shown: αβ-unsaturated acid chlorides are reduced only to αβ-unsaturated aldehydes; no dehalogenation of aromatic halides occurred; ortho-substituted acyl halides gave good yields of aldehydes, although the sterically-crowded pivaloyl chloride gave only a modest yield of pival-aldehyde.

Halides are useful functional groups in synthesis so that the stabilities of dodecyl chloride, bromide, and iodide to the reducing agent are particularly encouraging; the lack of reactivity of benzyl chloride is noteworthy.

From the variety of reducible functional groups which survives this new reducing agent, it appears to be markedly selective and, in this respect, compares favourably with other reported direct reductions of acyl halides to aldehydes. For example, reduction of acyl halide with triphenyltin hydride gives variable yields of esters as well as aldehyde, and exchange of halogen for hydrogen is observed in some halogenated acyl halides.[16]

The present procedure using cadmium(II)–modified sodium tetrahydroborate is simple and convenient. The reagent can be prepared in bulk and stored at 0 °C, and all products from hydrolysis after reduction are water-soluble and are not extracted into organic solvents.
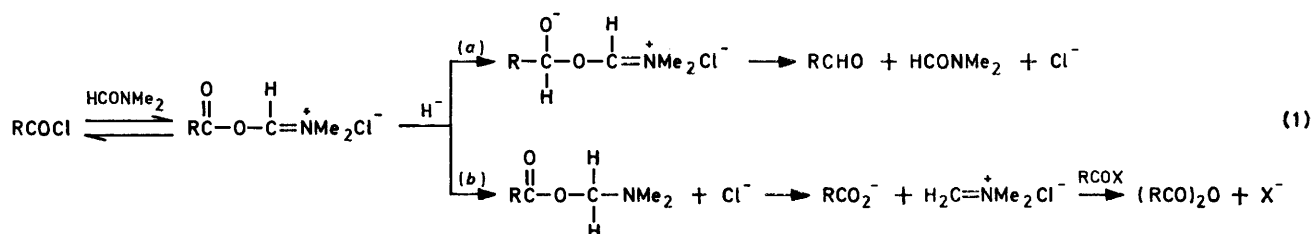
Recently, two groups have reported the direct reduction of acid chlorides to aldehydes by use of bis-(triphenylphosphine)copper(I) tetrahydroborate.[17a,b] Yields of aldehydes were similar to those reported here but the utility of this triphenylphosphine-complexed tetrahydroborate suffers from its high molecular weight, and the more laborious work-up needed to remove the triphenylphosphine from reduction products. In one of these last reports,[17a] it was necessary to add up to two molar equivalents extra of triphenylphosphine to effect reduction and suggests an acyl–triphenylphosphine complex may actually be the species reduced, similar to our acyl–DMF complex.

Stable acyl–DMF complexes have been isolated from acyl bromides,[18] whereas acyl chlorides yield only a small equilibrium percentage of complex in solution. From this point of view, it seemed that acyl bromides might give higher yields of aldehydes than acyl chlorides. In fact, yields of aldehydes were about the same for bromides and chlorides, and the sensitivity of the former to atmospheric moisture made them less convenient to use.

Zinc tetrahydroborate, either prepared separately or in situ by metathetical reaction from zinc chloride and sodium tetrahydroborate, gave inferior yields of aldehydes. Other attempted reductions in the presence of Pb^{2+}, Fe^{2+}, or Hg$^+$ salts, either in catalytic or stoicheiometric amounts, led either to reduction to metal or to very inferior yields of aldehyde; debromination of

steroidal bromoketones by sodium tetrahydroborate in the presence of catalytic quantities of Pb^{2+} or Cu^{2+} has been reported.[19]

Two minor products from these reductions were noted. The first was the alcohol resulting from over-reduction of acyl chloride and the second was the acid anhydride. The reduction is envisaged as proceeding according to equation (1) in which the intermediate acyl–DMF complex can react with ' hydride ', either at the carbonyl group, releasing DMF and giving aldehyde (1a), or at the ' immonium carbon ', releasing a carboxylate anion;

formamide were removed by stirring with solid potassium hydroxide, and the decanted solvent dried either by azeotroping with benzene before distillation or by distillation from calcium hydride. Acid chlorides were prepared by standard methods from the acid and thionyl chloride [24] or from the acid and oxalyl chloride; [25] acid bromides were prepared by the latter method from oxalyl bromide. Dodecyl chloride [26] and dodecyl bromide [27] were prepared from dodecan-1-ol by treatment with phosphorus(III) chloride or bromide. Dodecyl iodide was prepared by reacting the bromide with NaI in acetone.

After all the reductions, aldehyde was estimated by

$$RCOCl \underset{HCONMe_2}{\rightleftharpoons} RC\overset{\displaystyle O}{\overset{\displaystyle \|}{-}}O-\overset{\displaystyle H}{\underset{}{C}}=\overset{+}{N}Me_2Cl^- \xrightarrow{H^-} \begin{cases} (a) \quad R-\overset{\displaystyle O^-}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}}}-O-\overset{\displaystyle H}{\overset{\displaystyle |}{C}}=\overset{+}{N}Me_2Cl^- \longrightarrow RCHO + HCONMe_2 + Cl^- \\[2em] (b) \quad RC\overset{\displaystyle O}{\overset{\displaystyle \|}{-}}O-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}}}-NMe_2 + Cl^- \longrightarrow RCO_2^- + H_2C=\overset{+}{N}Me_2Cl^- \xrightarrow{RCOX} (RCO)_2O + X^- \end{cases}$$

(1)

reaction of the carboxylate anion with acyl halide or acyl–DMF complex would yield the anhydride (1b).

In equation (1), the nature of the hydride species is not specified. On preparation of the tetrahydroborate reducing solution from $CdCl_2 \cdot 1.5DMF$ and $NaBH_4$, no precipitate of NaCl was observed, suggesting that a complex anion had been formed. Similar behaviour has been reported for the metathetical reaction of $NaBH_4$ and $AlCl_3$ in which, again, no NaCl precipitated.[20] The i.r. spectrum of $NaBH_4$ in DMF showed a strong absorption at $2\ 230\ cm^{-1}$, characteristic of ionic tetrahydroborates. Addition of $CdCl_2$ caused this band to disappear and two new, weaker bands at $2\ 100$ and $2\ 400$ cm^{-1} to appear. These bands correspond closely with published data for covalent tetrahydroborates [21] and, along with the lack of a precipitate of NaCl, suggest the formation of a complex salt such as $Na[CdCl(BH_4)_2]$ or $Na_2[CdCl_2(BH_4)_2]$ as the reductant, rather than $Cd[BH_4]_2$. When a large excess of diethyl ether or carbon tetrachloride was added to the reducing agent prepared in acetonitrile, a white precipitate appeared. However, this precipitate was not NaCl and contained much of the hydride reducing power.

The above work indicates that the selectivity of the cadmium-modified reducing agent is based on two factors. Firstly, the tetrahydroborate is much less active than sodium tetrahydroborate (it does not reduce aldehydes significantly) and secondly, the acyl–DMF complex is much more reactive than acyl halide alone. The two factors together give a reducing agent capable of producing aldehydes only from acyl halides and incapable of reducing other functional groups.

EXPERIMENTAL

Anhydrous metal chlorides were obtained by refluxing the hydrated salt with acetyl chloride.[22] Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) was crystallized from dimethylformamide to give $CdCl_2 \cdot 1.5DMF$.[23] Acidic impurities in dimethyl-

precipitation as the 2,4-dinitrophenylhydrazone or from the CHO resonance in the n.m.r. spectrum compared with C_6H_5 and CH_2OH resonances. The 2,4-dinitrophenylhydrazones were recrystallized and consistently indicated 5—10% lower yields than did the n.m.r. spectra of the total crude reaction product before reaction with 2,4-dinitrophenylhydrazine; the yields reported in the Table are the lower values based on the crystallized 2,4-dinitrophenylhydrazones.

Reductions with Tetrahydroborates produced metathetically and used in situ.—(a) *With copper*(II) *chloride*. Sodium tetrahydroborate (50 mg; 1.3 mmol) was dissolved in dimethylformamide (10 ml) and cooled to *ca.* $-10\ ^\circ C$. Anhydrous copper(II) chloride (100 mg; 0.75 mmol) in DMF (6 ml) was added to the tetrahydroborate with stirring. Slight effervescence was noted and a brown colour developed. After 10 min, benzoyl chloride (100 mg; 0.7 mmol) in DMF (2 ml) was added and, after 3 min, a large excess of water. The subsequent black precipitate was dissolved in dilute HCl and extracted with ether to afford benzaldehyde, precipitated as its 2,4-dinitrophenylhydrazone (46% yield). Benzoic acid (20 mg; 20%) was recovered from sodium hydrogencarbonate washings of the original ether extract. The balance of material was benzoic anhydride (^1H n.m.r. and very characteristic i.r.).

When the above experiment was repeated in hexamethylphosphoramide or dimethylacetamide as solvent, increased yields of benzaldehyde were found but also considerable over-reduction to benzyl alcohol.

(b) *With copper*(II) *chloride and co-ordinating ligands*. The above reduction (a) in the presence of 2—3 mmol proportion of either triethylamine, triethyl phosphite, or triphenylphosphine afforded respectively 30, 40—50, and 63% yields of benzaldehyde.

(c) *With copper*(I) *chloride*. The procedure was as in (a) giving a 63% yield of benzaldehyde at $-5\ ^\circ C$; the balance of material was mostly benzyl alcohol and benzoic anhydride.

(d) *With copper*(I) *chloride without DMF*. Repetition of reaction (c) in acetonitrile without DMF gave back benzoyl chloride at $-5\ ^\circ C$ but, at $60\ ^\circ C$ for 5 min, the benzoyl chloride was reduced completely to benzyl alcohol.

(e) *With copper*(I) *chloride and a co-solvent.* To the reducing agent prepared as in (c) was added diethyl ether (or tetrahydrofuran or carbon tetrachloride; 30 ml). Reaction with benzoyl chloride gave yields of benzaldehyde similar to those obtained without co-solvent.

(f) *With* CdCl$_2$·1.5DMF. To a solution of sodium tetrahydroborate (76 mg; 2 mmol) in acetonitrile (10 ml) and hexamethylphosphoramide (0.5 ml) was added CdCl$_2$·1.5DMF (365 mg; 1.25 mmol) and the mixture stirred for 5 min at −5 °C. To the slightly opaque solution was added benzoyl chloride (280 mg; 2 mmol) rapidly with stirring. After 5 min, dilute HCl was added slowly (effervescence) and the reaction product extracted with diethyl ether to yield benzaldehyde (76%). From duplicate experiments, ^{1}H n.m.r. spectroscopy indicated a yield of 80—90% with the residual material being benzyl alcohol. Many of the aldehydes reported in the Table were obtained in this way.

Use of hexamethylphosphoramide could be obviated by use of diglyme as co-solvent, or by use of an excess of DMF. For example, to a stirred suspension of CdCl$_2$ (4.64 g; 25 mmol) in acetonitrile (25 ml) was added a solution of NaBH$_4$ (0.76 g; 20 mmol) in DMF (5 ml) and acetonitrile (40 ml) at 0 to −5 °C over a period of 10 min; stirring was continued for a further 10 min. The solution was cooled to *ca.* −30 °C and a solution of ethyl *cis*-2-chlorocarbonyl-cyclopropanecarboxylate (3.53 g; 20 mmol) in acetonitrile (25 ml) was added over a period of 15 min, and then stirred for a further 10 min to give ethyl *cis*-2-formylcyclopropanecarboxylate (50% yield as its 2,4-dinitrophenylhydrazone).

(g) *With* ZnCl$_2$. To a stirred suspension of ZnCl$_2$ (3.4 g) in acetonitrile (25 ml) at 0 °C was added NaBH$_4$ (760 mg) dissolved in a mixture of DMF (5 ml) and acetonitrile (40 ml). After 10 min, the solution was cooled to −35 °C and benzoyl chloride (2.81 g) in acetonitrile was added over a period of 15 min. Stirring was continued for 10 min and the reaction mixture was worked up as in (f) to give a 40% yield of benzaldehyde.

Reduction with pre-prepared Zn[BH$_4$]$_2$.—An ether solution containing Zn[BH$_4$]$_2$ (0.13 mmol ml^{-1}) was prepared.[13] As addition of DMF to this solution caused a fine white precipitate to appear and the resulting solution did not reduce benzoyl chloride, an equal volume of acetonitrile was added to any volume of the ethereal Zn[BH$_4$]$_2$ and the ether removed on a rotary evaporator at 5—10 °C to give a clear solution. This solution (7.7 ml; 1 mmol) was cooled to −5 °C and DMF (150 mg; 2 mmol) was added with stirring. Benzoyl chloride (280 mg; 2 mmol) in diethyl ether (2—3 ml) was added and the mixture was stirred at 0 °C for 20 min to give a 53% yield of benzaldehyde; most of the remaining product was benzoic anhydride.

Reduction of Acyl Bromides.—This was performed as in procedure (f) above.

Reduction of Alkyl Halides.—NaBH$_4$ (1 mmol) and CdCl$_2$·1.5DMF (0.51 mmol) were stirred in acetonitrile (6 ml) and diglyme (0.5 ml) at −5 °C. To the slightly opaque solution was added n-dodecyl chloride (1 mmol) in acetonitrile (3 ml) and the mixture stirred for 5 min at −5 °C. Addition of dilute HCl and extraction with diethyl ether gave back all the dodecyl chloride. Similarly, no reaction was observed with n-dodecyl bromide, n-dodecyl iodide, and benzyl chloride.

REFERENCES

[1] This work now forms Part 8 of a series on metal-assisted reactions: Part 1; *J.C.S. Perkin I*, 1975, 1300; Part 2, *J.C.S. Perkin I*, 1975, 1216; Part 3, *Synthesis*, 1976, 685; Part 4, *J. Chem. Research* (S), 1977, 117; Part 5, *J.C.S. Perkin I*, 1977, 443; Part 6, *Tetrahedron*, 1978, **34**, 213; Part 7, *J.C.S. Chem. Comm.*, 1978, 354.

[2] For leading references see M. N. Rerick, in ' Reduction,' ed. R. L. Augustine, Arnold, London, 1968, ch. 1; H. C. Brown, ' Boranes in Organic Chemistry,' Cornell University Press, Ithaca, 1972, pp. 209—226.

[3] See *e.g.* (a) E. Schenker in ' Newer Methods of Preparative Organic Chemistry,' vol. 4, ed. W. Foerst, Verlag Chemie, 1968, p. 196; (b) E. R. H. Walker, *Chem. Soc. Rev.*, 1976, **5**, 23.

[4] (a) M. Pesez and J.-F. Burtin, *Bull. Soc. chim. France*, 1959, 1996; T. Satoh, S. Suzuki, Y. Suzuki, Y. Miyaji, and Z. Imai, *Tetrahedron Letters*, 1969, 455; (b) T. Nielson, H. C. S. Wood, and A. G. Wylie, *J. Chem. Soc.*, 1962, 371; R. L. Edwards and N. Kale, *J. Chem. Soc.*, 1964, 4084.

[5] R. A. Egli, *Helv. Chim. Acta*, 1968, **51**, 2090.

[6] T. Satoh, S. Suzuki, T. Kikuchi, and T. Okada, *Chem. and Ind.*, 1970, 1626.

[7] H. C. Brown and K. Ichikawa, *J. Amer. Chem. Soc.*, 1961, **83**, 4372; H. C. Brown, E. J. Mead, and B. C. Subba Rao, *ibid.*, 1955, **77**, 6209.

[8] For a review see E. Mosettig and R. Mozingo, *Org. Reactions*, 1948, **4**, 362.

[9] H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, 1958, **80**, 5372; H. C. Brown and B. C. Subba Rao, *ibid.*, 1958, **80**, 5377.

[10] E. Wiberg and W. Henzle, *Z. Naturforsch.*, 1952, **7b**, 582 (*Chem. Abs.*, 1953, **47**, 2619f).

[11] S. W. Chaiken and W. G. Brown, *J. Amer. Chem. Soc.*, 1949, **76**, 122.

[12] For references see, D. E. Horning and J. M. Muchowski, *Canad. J. Chem.*, 1967, **45**, 1247.

[13] For a preparation of zinc borohydride see, W. J. Gensler, F. Johnson, and A. D. B. Sloan, *J. Amer. Chem. Soc.*, 1960, **82**, 6074; for cadmium borohydride, see ref. 7.

[14] R. C. Paul, S. Singh, and B. R. Sneenathan, *Indian J. Chem.*, 1964, **2**, 97 (*Chem. Abs.*, 1964, **61**, 1351g).

[15] R. A. W. Johnstone and R. P. Telford, *J.C.S. Chem. Comm.*, 1978, 354.

[16] For leading references see H. G. Kuivila in 'Advances in Organometallic Chemistry,' eds. F. G. A. Stone and R. West, Academic Press, New York, 1964, p. 47.

[17] (a) G. W. J. Fleet, C. J. Fuller, and P. J. C. Harding, *Tetrahedron Letters*, 1978, 1437; (b) T. N. Sorrell and R. J. Spillane, *ibid.*, 1978, 2473.

[18] H. K. Hall, *J. Amer. Chem. Soc.*, 1956, **78**, 2717.

[19] T. Goto and Y. Kishi, *Tetrahedron Letters*, 1961, 513.

[20] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1955, **78**, 2582.

[21] T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.

[22] A. R. Pray, *Inorg. Synth.*, 1957, **5**, 154.

[23] R. C. Paul, S. Singh, and B. R. Sneethan, *Indian J. Chem.*, 1964, **2**, 97.

[24] See *e.g.*, J. Munch-Petersen, *Org. Synth.*, Coll. Vol. 4, p. 715.

[25] See *e.g.*, G. Stork and F. M. Clarke, *J. Amer. Chem. Soc.*, 1961, **83**, 3114.

[27] J. W. Oldham and A. R. Ubbelhode, *J. Chem. Soc.*, 1938, 201.

[27] A. I. Vogel, *J. Chem. Soc.*, 1943, 644.

[28] N. R. Campbell, *Analyt*, 1936, **61**, 391.

[29] A. Sisti, J. Burgmaster, and M. Fudim, *J. Org. Chem.*, 1962, **27**, 279.

[30] R. F. Smith, J. A. Albright, and A. M. Waring, *J. Org. Chem.*, 1966, **31**, 4100.

[31] O. L. Brady and S. G. Jarrett, *J. Chem. Soc.*, 1950, 1021.

[32] A. T. Shulgin, *J. Medicin. Chem.*, 1966, **9**, 445.

[33] A. C. Cope, N. A. Nelson, and D. S. Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 1100.

[34] C. F. H. Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955.

[35] I. Heilbron, E. R. H. Jones, R. W. Richardson, and F. Sondheimer, *J. Chem. Soc.*, 1949, 737.

[36] A. I. Meyers, A. Nabeya, M. W. Adickes, I. R. Politzer, G. R. Malone, A. C. Korelsky, R. L. Nolan, and R. C. Portnoy, *J. Org. Chem.*, 1973, **38**, 36.

[37] C. L. Wilson, *J. Amer. Chem. Soc.*, 1947, **69**, 3002.