Possible Pathways for the Reduction of Carboxylic Acids by Diborane; the Reductions of Carboxylic and Mixed Anhydrides

By ANDREW PELTER,* M. G. HUTCHINGS, T. E. LEVITT, and K. SMITH
(*Department of Chemistry, The University, Manchester* M13 9PL)

Summary Two new reactions have been defined in the interactions of diborane with carboxylic acids: probable pathways of reduction of various acids are indicated, that of benzoic acid being very solvent sensitive.

REDUCTION of a carboxylic acid by diborane has been shown to proceed *via* uncharacterised species, possibly triacyloxyboranes (I) which are rapidly reduced (Equation 1).[1] It was noted however[1] that the existence of triacetoxyborane was the subject of some dispute, its dismutation to acetic anhydride and oxybisdiacetoxyborane (III; R = Me) *via* route (2) having been suggested.[2,3]

$$6RCO_2H + B_2H_6 \rightarrow \underset{(I)}{2(RCO_2)_3B} + 6H_2 \xrightarrow{2B_2H_6} 2(RCH_2O)_3B \qquad (1)$$

$$2(RCO_2)_3B \rightarrow \underset{(II)}{(RCO)_2O} + \underset{(III)}{[(RCO_2)_2B]_2O} \qquad (2)$$

The dismutation of triacyloxyboranes was of interest to us in connection with the mechanism of amide formation from carboxylic acids and amino-boranes[4-6] and therefore the reduction was further investigated.

If reduction proceeded *via* pathway 2, then the carboxylic anhydrides (II) and the mixed anhydrides (III) should be reduced by diborane at a rate comparable to that of the acids themselves. The derivatives (II) and (III) from benzoic and n-hexanoic acids were synthesised independently[7] and were satisfactorily reduced (Table 1), with an excess of diborane corresponding to that used by previous workers,[1] *i.e.* $(RCO)_2O : B_2H_6 = 1:1$; $[RCO_2)_2B]_2O : B_2H_6 = 1:2$.

TABLE 1*

Yields of alcohols in diborane reductions

	R = Ph	R = C_5H_{11}
Acid	83% (1 hr.)	77% (15 min.)
(II)	82% (1 hr.)	94% (20 min.)
(III)	97% (1 hr.)	91% (10 min.)

* All reductions carried out in tetrahydrofuran (THF). Yields are of isolated purified products.

In addition, acetic anhydride was reduced rapidly and completely to ethanol whilst oxybisdiacetoxyborane (III; R = Me) also gave ethanol in 10 min., though in this case the product was not isolated but analysed by g.l.c.

An artificial mixture (1 : 1) of (II) and (III) (R = Me) was reduced by diborane, the reductions of each species being of the same order, as indicated by the separate reductions, and no autocatalytic effects were observed.

The diborane reductions of carboxylic anhydrides (II) and oxybisdiacyloxyboranes (III) have not, to our knowledge, previously been reported. The former reduction in particular is of interest due to the complete contrast shown with the reported very slow reduction of an acid chloride.[1,8] Presumably reaction occurs because the carboxylic anhydride contains formally one good donor carbonyl group and after co-ordination to borane, reduction both internal and external may occur.[10,11]

Whether the dismutation (Equation 2) *did* occur under the reaction conditions was studied by mixing the reagents dissolved in THF in the ratio carboxylic acid : diborane 6 : 1. The evolution of *ca.* 90% of the theoretical quantity of hydrogen (Equation 1) together with the appearance of bands at ν_{max} 1620 and 1720 cm.$^{-1}$ was taken as evidence for the initial formation of (I).[7,9]

It can be seen (Table 2) that for the simple aliphatic acids hydrogen evolution was complete in all cases, but the rates of dismutation of (I) varied considerably. In the case of n-hexanoic acid it was almost instantaneous at room temperature but became much slower with decreasing chain length. Pivalic acid always gave *ca.* 80% theoretical hydrogen evolution and showed no tendency to yield carboxylic anhydride.

TABLE 2

Acid, RCO_2H	H_2 evolution	Carboxylic anhydride appearance
R = Me	93% (30 min.), 96% (1 hr.), 99% (1·5 hr.)	>1 hr.
Et	96% (1 hr.)	>1 hr.
Pr^n	96% (1 hr.)	1 hr.
Bu^n	97% (30 min.)	30 min.
$n\text{-}C_5H_{11}$	100% (5 min.)	Instantaneous and complete
Pr^i	97% (30 min.)	*ca.* 1 hr.
Bu^t	80%	None

The case of benzoic acid was very interesting as both hydrogen evolution and dismutation were solvent dependant (Table 3). Although it has been stated that the evolution of hydrogen from diborane in THF by benzoic acid is quantitative according to Equation 1,[1] in our hands numerous experiments always gave 65—67% theoretical. Even more surprisingly, addition of dry acetic acid, water, or dilute hydrochloric acid did not lead to further hydrogen evolution. Work-up of the reaction after 24 hr. gave benzoic acid quantitatively, no benzaldehyde or benzyl alcohol being detectable. Only on addition of water (1) and concentrated hydrochloric acid (3) was the extra hydrogen evolved (*i.e.* 66 → 89%; 65 → 95%).

TABLE 3

Addition of diborane to benzoic acid (1 : 6)

Solvent	H_2 evolution	Dismutation
THF	65% (50 min.)	None
	67% (5 hr.)	"
Diglyme–THF (7 : 1)	66% (5 min.), 91% (1 hr.)	"
Benzene–THF (7 : 1)	94% (5 min.)	Rapid and complete
	95% (5 min.)	"

When diborane (1 mol.) was added to benzoic acid (4 mol.) in THF, hydrogen evolution was quantitative as would be expected. The evidence points to the existence of a species of stoicheiometry $(PhCO_2)_2BH$ uniquely stabilised in THF, a conclusion supported by ^1H n.m.r. evidence.

In diglyme–THF (7 : 1), hydrogen evolution was complete within 1 hr. but there was no evidence of dismutation, whereas in a predominantly benzene solvent, both hydrogen evolution and dismutation were complete in 5 min., the products being isolated and characterised.

Thus several pathways are open for the diborane reduction of carboxylic acids. The lower aliphatic acids in THF form triacyloxyboranes (I) which may be further reduced, whilst these products derived from higher aliphatic acids rapidly dismute and may be reduced *via* (II) and (III). In THF as solvent, benzoic acid never reaches the triacyloxyborane stage but would be reduced as a diacyloxyborane. In diglyme however benzoic acid would be reduced through tribenzoyloxyborane (I; R = Ph).

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[1] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1960, **82**, 681.
[2] T. Ahmad and M. J. Khundkar, *Chem. and Ind.*, 1954, 284.
[3] W. Gerrard and E. F. Mooney, *Chem. and Ind.*, 1958, 227.
[4] P. Nelson and A. Pelter, *J. Chem. Soc.*, 1965, 5142.
[5] T. E. Levitt and A. Pelter, *Nature*, 1966, **211**, 299.
[6] A. Pelter and T. E. Levitt, *Tetrahedron*, in the press.
[7] T. E. Levitt, Ph.D. Thesis, Manchester University, 1969.
[8] H. C. Brown and W. Korytnyk, *J. Amer. Chem. Soc.*, 1960, **82**, 3866.
[9] L. A. Duncanson, W. Gerrard, M. F. Lappert, H. Pyszora, and R. Shafferman, *J. Chem. Soc.*, 1958, 3652.
[10] J. Klein and E. Dunkelblum, *Tetrahedron*, 1967, **23**, 205.
[11] J. J. Bloomfield and S. J. Lee, *J. Org. Chem.*, 1967, **32**, 3919.