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XXXIII *. PROTONOLYSIS OF TRIETHYLBORANE WITH CARBOXYLIC ACIDS **

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Summary

The hydrolysis of triethylborane with water proceeds very slowly at room temperature, unaffected by hydrochloric acid, but inhibited by sodium hydroxide. Acetic acid, however, removes the first ethyl group rapidly, followed by a slower removal of the second. The protonolysis of the third ethyl group requires elevated temperatures. The unusual reactivity of carboxylic acid toward protonolysis of triethylborane is attributed to the presence of both acidic and basic sites in close proximity. The effect of added reagents is also studied. Thus, bases, such as pyridine, inhibit the removal of the first ethyl group, whereas, hydroxylic solvents, water, and strong acids and bases hinder protonolysis of the second ethyl group.

Introduction

Trialkylboranes are remarkably stable toward water [1,2]. The presence of inorganic acids has very little effect [3], whereas, anhydrous carboxylic acids protonolyze them readily at room temperature [2,4] with the cleavage of two alkyl groups [5]. Consequently, the reaction of organoboranes with carboxylic acids is a convenient method for the conversion of alkenes into the corresponding saturated hydrocarbons via hydroboration. Following the initial report on the use of hydroboration-protonolysis as a route for the non-catalytic hydrogenation of alkenes [5,6], a detailed kinetic and mechanistic study of the cleavage of carbon–boron bond by carboxylic acids was reported by Dessy [7,8]. This study confirmed the importance of coordination in the protonolysis reaction, which was proposed earlier [9] (eq. 1).

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* For part XXXII, see H.C. Brown and T. Imai, J. Am. Chem. Soc., in press.

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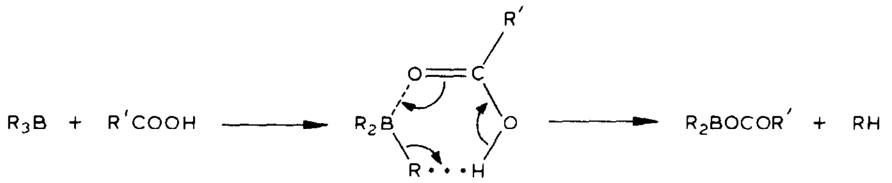

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In order to understand better the various factors involved in the protonolysis of organoboranes with carboxylic acids, we undertook to examine the reaction of a simple model compound, triethylborane, with representative carboxylic acids and to establish the effect of different reagents on this reaction.

Results and discussion

In general, the reaction of triethylborane with representative carboxylic acids was examined at 25°C, utilizing high vacuum techniques. The protonolysis of the ethyl groups was followed conveniently by measuring the ethane gas evolved. As shown in Table 1, simple carboxylic acids possess a unique ability to cleave two ethyl groups from triethylborane at 25°C.

All of the five acids examined reacted with comparable ease. It is clear that protonolysis takes place in three stages of increasing difficulty: the removal of the first ethyl group is very rapid, followed by a slower removal of the second. The third ethyl group is not removed at any reasonable rate at 25°C by any of the acids studied. This is consistent with the decreased ability of the boron moiety to coordinate with carboxylic acid when the ethyl groups are successively replaced with acyloxy groups (eqs. 2 and 3).

$$(C_2H_5)_3B + RCOOH \rightarrow (C_2H_5)_2BO_2CR + C_2H_6 \qquad (2)$$

$$(C_2H_5)_2BO_2CR + RCOOH \rightarrow C_2H_5B(O_2CR)_2 + C_2H_6 \qquad (3)$$

As a result of these preliminary investigations, acetic acid was chosen as a standard acid for further studies.

Effect of solvent

Protonolysis was carried out in several selected solvents. The reaction proceeded more rapidly in acetic anhydride and nitrobenzene. However, in dimethyl formamide

TABLE 1

REACTION OF TRIETHYLBORANE WITH CARBOXYLIC ACIDS AT 25°C [a]

Acid	Ethane liberated (mmol/mmol of Et_3B)				
Time:	1 h	3 h	6 h	10 h	20 h
Acetic	1.36	1.82	1.95	1.95	1.98
Propionic	1.12	1.46	1.80	1.87	1.91
Isobutyric	1.05	1.30	1.53	1.70	1.78
Octanoic	1.09	1.35	1.58	1.78	1.86
Trifluoroacetic	1.32	1.80	1.97	1.99	2.00

[a] Carboxylic acid (2.0 ml) and Et_3B (0.5 mmol) were mixed and the amount of C_2H_6 liberated at 25°C was measured with time.

TABLE 2

REACTION OF TRIETHYLBORANE WITH ACETIC ACID IN VARIOUS SOLVENTS AT 25°C [a]

Solvent	Ethane liberated (mmol/mmol of Et_3B)				
Time:	1 h	3 h	6 h	10 h	20 h
Diglyme	1.08	1.35	1.71	1.94	1.97
Acetic anhydride	1.14	1.47	1.83	1.85	1.86
Decalin	1.16	1.46	1.71	1.80	1.83
Ethylene glycol	0.99	0.99	0.99	0.99	0.99
Nitrobenzene	1.21	1.55	1.79	1.87	1.90
Dimethyl formamide	1.00	1.00	1.00	1.00	1.00

[a] Et_3B (0.5 mmol), acetic acid (1.0 ml) and the solvent indicated (1.0 ml) were mixed at 25°C.

and ethylene glycol, only one ethyl group was protonolyzed. Ethylene glycol hinders further protonolysis by converting the intermediate monoacetate into a less reactive borinate ester [10]. Dimethyl formamide probably coordinates strongly with the monoacetate, making it resistant to further protonolysis. In decalin and diglyme, protonolysis proceeds with comparable rates. Diglyme is presumably too weak a base to coordinate with Et_2BOAc. The results are summarized in Table 2.

Effect of temperature

At 25°C, most carboxylic acids protonolyze one ethyl group rapidly (< 1 h) and a second group more slowly (10–20 h) (Table 1). The third ethyl group does not undergo protonolysis under these conditions. However, at higher temperatures, the third ethyl group also undergoes protonolysis. For example, in refluxing acetic acid (120°C), 2.18 ethyl groups are protonolyzed in 24 h, while propionic acid removes 2.79 ethyl groups under similar conditions. The data presented in Table 3 indicate that at higher temperatures the third alkyl group can be conveniently protonolyzed. Consequently, it is customary to heat the organoborane in a higher boiling acid, such as propionic or isobutyric acid, under reflux for complete protonolysis [11].

Effect of added reagents

In order to understand the effect of acidic, basic, and neutral reagents on the

TABLE 3

EFFECT OF TEMPERATURE ON THE PROTONOLYSIS OF TRIETHYLBORANE [a]

Acid	Temp. (°C)	Time (h)	Ethane evolved (mmol/mmol of Et_3B)
Acetic	100	24	2.00
	120	24	2.18
Propionic	100	24	2.30
		48	2.50
	120	24	2.79
	140	7.6	2.94
Isobutyric	100	24	2.10

[a] Et_3B, 0.5 mmol, and carboxylic acid, 2.0 ml.

TABLE 4

EFFECT OF WATER ON THE PROTONOLYSIS OF TRIETHYLBORANE AT 25°C [a]

Amount of water (mmol)	Ethane evolved (mmol/mmol of Et_3B)				
Time:	1 h	3 h	6 h	10 h	20 h
2.0	1.0	1.0	1.0	1.0	1.0
1.0	1.0	1.0	1.0	1.0	1.0
0.4	1.0	1.0	1.0	1.0	1.0
0.2	1.0	1.0	1.05	1.08	1.16
0.1	1.01	1.10	1.22	1.38	1.72
0	1.36	1.82	1.95	1.95	1.98

[a] Et_3B (0.5 mmol) was treated with acetic acid (2.0 ml) containing desired amounts of water.

protonolysis of Et_3B with acetic acid, the reaction was carried out under similar conditions and the required amount of chosen reagent was taken in acetic acid.

Effect of water

The presence of water does not affect the cleavage of the first ethyl group. However, cleavage of the second ethyl group is inhibited for water-to-borane ratios greater than 0.5 (Table 4). This can be accounted for in terms of the hydrolysis of the intermediate, monoacetate (eqs. 4 and 5) [10].

$$(C_2H_5)_2BOCOCH_3 + H_2O \rightarrow (C_2H_5)_2BOH + CH_3COOH \quad (4)$$

$$(C_2H_5)_2BOH + (C_2H_5)_2BOCOCH_3 \rightarrow (C_2H_5)_2BOB(C_2H_5)_2 + CH_3COOH \quad (5)$$

Both the borinic acid and its anhydride are expected to resist further attack by acetic

TABLE 5

EFFECT OF ACIDS AND BASES ON THE PROTONOLYSIS OF Et_3B WITH ACETIC ACID AT 25°C [a]

Reagent	Ethane evolved (mmol/mmol of Et_3B)				
Time:	1 h	3 h	6 h	10 h	20 h
Acetic anhydride	1.35	1.74	1.89	1.89	1.89
Isobutyric acid	1.25	1.70	1.99	1.99	2.00
Benzoic acid	1.27	1.80	1.95	1.95	1.98
Maleic acid	1.20	1.52	1.81	1.91	1.91
Boron trifluoride	1.50	1.83	1.92	1.93	2.00
Trifluoroacetic acid	1.06	1.14	1.20	1.27	1.44
Oxalic acid	0.98	0.99	0.99	1.00	1.00
Salicylic acid	0.98	1.00	1.02	1.02	
Picolinic acid	1.00	1.00	1.00	1.00	
Methanesulfonic acid	1.00	1.02	1.05	1.09	1.19
Sulfuric acid	1.03	1.08	1.14	1.18	1.29
Pyridine	0.06	0.15	0.27	0.39	0.63
Sodium acetate	1.05	1.11	1.15	1.20	1.33

[a] Triethylborane (0.5 mmol) was reacted with 2.0 ml of a 1 *M* solution of the desired reagent in acetic acid.

TABLE 6

EFFECT OF ADDED CATIONS AND ANIONS ON THE PROTONOLYSIS OF Et_3B WITH ACETIC ACID AT 25°C [a]

Salt	Ethane evolved (mmol/mmol of Et_3B)				
Time:	1 h	3 h	6 h	10 h	20 h
Sodium fluoride	1.02	1.07	1.13	1.20	1.39
Sodium tetrafluoroborate	1.11	1.37	1.71	1.87	1.89
Barium acetate	1.03	1.07	1.10	1.11	1.28
Mercuric acetate [b]	0.82	1.04	1.15	1.20	1.27
Nickel(II) acetate	1.02	1.03			
Cadmium acetate	1.14	1.47	1.82	1.86	
Silver acetate	1.12	1.53		1.77	1.77

[a] A 2.0-ml solution of the desired salt (1 *M*) in acetic acid was treated with 0.5 mmol of Et_3B. [b] Only 0.1 *M* solution of $Hg(OAc)_2$ in acetic acid was used.

acid, owing to the lower Lewis acidities of boron centers in these derivatives compared with monoacetate.

It appears that such inhibition of protonolysis beyond the removal of one ethyl group might take place in other hydroxylic reagents via the formation of borinic esters, in conformity with the effects observed with ethylene glycol and salicylic acid.

Effect of acids and bases

In general, the removal of the second ethyl group was inhibited by strong acids and bases. In the presence of pyridine, even the removal of the first ethyl group is slow, apparently due to complexation of pyridine with Et_3B. Strong acids, such as sulfuric, methanesulfonic, oxalic and trifluoroacetic acid, inhibit the rate of reaction, while weak acids, such as isobutyric, benzoic and maleic acid, have no noticeable influence. Inhibition of picolinic acid is probably via complexation, as in the case for pyridine. Salicylic acid prevents the removal of the second ethyl group via the formation of the internal borinate complex. The presence of sodium acetate has little effect on the removal of the first ethyl group, but it prevents removal of the second. These results are summarized in Table 5.

Effect of added cations and anions

The rate of protonolysis of the second ethyl group is inhibited by barium acetate, nickel acetate, mercuric acetate, and sodium fluoride. These salts probably suppress the dissociation and ionization of acetic acid dimer, thus decreasing the concentration of reactive acetic acid species. However, cadmium and silver acetates had no large effect on the rate of protonolysis (Table 6).

Conclusion

Protonolysis of triethylborane with anhydrous carboxylic acids proceeds at room temperature to cleave only two ethyl groups. Removal of the third ethyl group can be accomplished at higher temperatures. Water, hydroxylic solvents, strong acids and bases inhibit the removal of the second ethyl group.

This study reveals practical conditions for the protonolysis of trialkylboranes. It is now possible to carry out protonolysis selectively for the removal of either one or two alkyl groups, if desired, by choosing appropriate reaction conditions.

Experimental

Materials

Triethylborane from Callery Chemicals was purified by repeated distillation. Acetic acid (Baker analyzed) was also distilled and a purity of 99.8% was determined from cooling curve data. All other liquid acids, anhydrides, bases and solvents were purified by distillation. Metal salts and solid acids were dried to a constant weight in vacuo.

Apparatus and techniques

All experiments were carried out in all-glass high vacuum system equipped with mercury float valves. Standard techniques were utilized as described elsewhere [12].

Reactions were carried out in a vessel containing a Teflon-covered magnetic stirring bar. The vessel was sealed onto a standard tapered joint for attaching to the reaction system. The reaction system consisted of the vessel, mercury float valve and manometer.

Analyses

The extent of reaction could be calculated at any time during the course of the reaction from the observed pressure in the system by comparing with a predetermined plot of pressure of ethane versus moles of ethane over acetic acid.

Reaction of triethylborane with water at room temperature

Triethylborane, 0.488 mmol, was condensed on 2.0 ml of degassed distilled water by means of a liquid nitrogen bath. The reaction vessel was warmed to room temperature and the reaction was allowed to proceed with stirring. The initial pressure in the system was 66 mm at 25°C. Slow evolution of ethane occurred, and after about 20 h, the pressure in the system remained sensibly constant. Ethane corresponding to 32% of the available ethyl groups was obtained on fractionation after 89 h.

Similarly, from triethylborane (0.602 mmol), hydrogen chloride (3.2 mmol), and 2.0 ml of water, the evolution of ethane proceeded slowly and the pressure in the system remained sensibly constant after about 20 h at room temperature. After 89 h, ethane (0.554 mmol) (30% of the ethyl groups) was obtained.

Similarly, with water containing sodium hydroxide (4.0 mmol), no appreciable change of pressure was observed in the reaction system, even after 89 h at room temperature.

Reaction of triethylborane with acetic acid

Triethylborane, (0.510 mmol, 26.5 mmHg, 32.5°C, 366.7 cc in the standard bulb) was condensed on 2.0 ml of acetic acid by means of a liquid nitrogen bath. The acetic acid had been degassed several times until a constant vapor pressure was observed (15.0 mmHg at 25°C). The reaction mixture was allowed to warm to room temperature. The first pressure reading was taken as soon as it reached above 15 mm. All of the readings were taken with the reaction vessel submerged in a bath held at 25°C.

After 20.1 h, the reaction mixture was frozen with a liquid nitrogen bath and the reaction system opened to the vacuum system. The ethane was then removed by fractionation, through a trap held at −78°C, into the standard bulb cooled to liquid nitrogen temperature. The standard bulb was warmed to room temperature and 0.992 mmol of ethane was found. This is equivalent to 64.8% reaction. The intermediate pressure reading was converted into percent reaction by means of a plot of pressure versus mmol of ethane over 2.0 ml of acetic acid at 25°C.

Effect of added reagents

All reactions were carried out as previously described in the reaction with acetic acid. All reaction mixtures consisted of triethylborane (0.5 mmol) and 2.0 ml of acetic acid solution (1 *M* in added reagent).

With boron trifluoride, hydrogen chloride, and insoluble metal salts, these were added to 2.0 ml of the acetic acid.

Effect of solvent

All reactions were carried out as described in the reaction with acetic acid. The reaction mixtures consisted of triethylborane, 1.0 ml of acetic acid and 1.0 ml of solvent.

Effect of temperature

Reactions were carried out in chosen carboxylic acids at the temperatures indicated. The amounts of ethane liberated were measured as described before.

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