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REACTION OF TRIALKYLBORANE WITH 1-ALKYNE AND LEAD(IV) ACETATE. A NEW REGIOSPECIFIC AND STEREOSPECIFIC ONE-POT SYNTHESIS OF ENOL ACETATES

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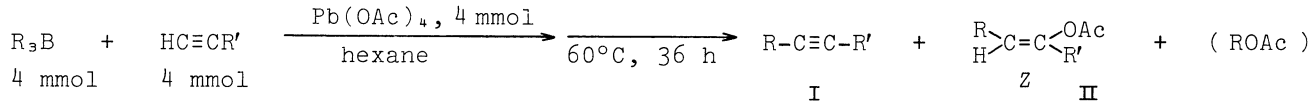
In the reaction of trialkylborane with 1-alkyne and lead(IV) acetate in hexane, one of the alkyl groups of trialkylborane migrated to the terminal carbon atom of the triple bond, giving regiospecifically an internal enol acetate and an internal alkyne as the main reaction products. The former compound had (Z)-configuration.

Among reactions of organoborane with oxidizing agent, the reaction of organoborane with lead(IV) acetate (L T A) is one of interesting classes. Trialkylboranes were reported to react with LTA to give the alkyl acetate by coupling between the alkyl group and the acetoxy group,[1] whereas 1-alkenyldialkylborane or its halo-substituted derivative, (1-halo-1-alkenyl)dialkylborane, gave 1,2-dialkylethene and its halo derivative respectively by an intramolecular migration of one alkyl group of the organoborane to the alkenyl carbon atom under the similar condition.[2] In the present paper we wish to report a new reaction of trialkylborane with 1-alkyne and LTA in which an internal enol acetate and an internal alkyne are formed regiospecifically and stereospecifically.

The addition of LTA to a solution of trihexylborane and 1-hexyne in hexane,[3] followed by subsequent stirring for 36 hr at 60°C, afforded a 40% yield of 5-dodecyne (**Ia**) and a 35% yield of (Z)-5-acetoxy-5-dodecene (**IIa**) along with a 7% yield of hexyl ethanoate. Similar results were also obtained by using tricyclopentylborane as the trialkylborane, or phenylethyne as the 1-alkyne (Scheme 1). Almost pure **I** and **II**



a, R= n-C_6H_{13} ; R'= n-C_4H_9	**Ia**, Y= 40%	**IIa**, Y= 35%	**Ia** + **IIa**, Y= 75%
b, R= c-C_5H_9 ; R'= n-C_4H_9	**Ib**, Y= 27%	**IIb**, Y= 49%	**Ib** + **IIb**, Y= 76%
c, R= n-C_6H_{13} ; R'= C_6H_5	**Ic**, Y= 36%	**IIc**, Y= 24%	**Ic** + **IIc**, Y= 60%
d, R= n-C_8H_{17} ; R'= n-C_4H_9			
e, R= n-C_4H_9 ; R'= C_6H_5			

Scheme 1

were easily separated from the reaction mixtures by a simple column chromatography in all cases examined.

Enol acetate has been used as an important synthetic intermediate in organic

syntheses.[4] For examining the synthetic utility of the reaction, we made several attempts to obtain I or II selectively. Although no remarkable improvement was realized both in the selectivity and in the yield, the ratio of I to II was altered to a certain extent by merely changing the ratio of the reactants. It is preferable to use an excess of the trialkylborane toward 1-alkyne for the predominant formation of I (Table 1). Some available synthetic methods for the internal alkynes by the

Table 1. Reaction[a] of 1-Alkynes and LTA with the Excess of Trihexylborane

1-Alkyne mmol	$(n\text{-}C_6H_{13})_3B$ mmol	LTA mmol	Product[b] Yield mmol (%)[c]		Total yield mmol (%)[c]
1-Hexyne			Ia	IIa	Ia + IIa
2	4	2	1.04 (52)	0.40 (20)	1.44 (72)
2	4	4	1.12 (56)	0.44 (22)	1.56 (78)
Phenylethyne			Ic	IIc	Ic + IIc
2	4	4	o.94 (47)	0.26 (13)	1.20 (60)

a) Carried out for 36 hr at 60°C. b) Alkyl ethanoate(about 20~60%) is formed besides these. c) Determined by glpc based on 1-alkyne employed.

organoborane have already been reported.[5] Therefore, this reaction concedes the utility to these methods.

On the contrary, the use of excesses of 1-alkyne and LTA toward trialkylborane led to the predominant formation of the enol acetate over the internal alkyne (Table 2).

Table 2. Reaction[a] of Trialkylboranes with the Excess of 1-Alkynes and LTA

R_3B, R= mmol	1-Alkyne mmol	LTA mmol	Product[b] Yield mmol (%)[c]		Total yield mmol (%)[c]
Hexyl	1-Hexyne		Ia	IIa	Ia + IIa
4	8	4	1.76 (44)	1.92 (48)	3.68 (92)
20	40	20	8.05 (40)[d]	8.92 (45)[d,e]	17.0 (85)
4	8	8	1.81 (45)	2.68 (67)	4.49 (112)[f]
c-Pentyl	1-Hexyne		Ib	IIb	Ib + IIb
4	8	8	1.12 (28)	3.45 (86)	4.57 (114)[f]
20	40	40	6.20 (31)[d]	17.8 (89)[d,e]	24.0 (120)[f]
Hexyl	Phenylethyne		Ic	IIc	Ic + IIc
4	8	8	1.68 (42)	2.12 (53)	3.80 (95)
Octyl	1-Hexyne		Id	IId	Id + IId
20	40	40	8.45 (42)[d]	14.6 (73)[d,e]	23.1 (115)[f]
Butyl	Phenylethyne		Ie	IIe	Ie + IIe
20	40	40	10.0 (50)[d]	14.1 (71)[d,e]	24.1 (121)[f]

a) Carried out for 36 hr at 60°C. b) Alkyl ethanoate (about 10%) from R_3B is formed besides these. c) Determined by glpc based on R_3B employed. d) Isolated by column chromatography. e) Isomeric purity of Z isomer is over 99%. f) Second alkyl group in R_3B seemed to take part in these reactions.

For example, 1.81 mmol(45% yield based on R_3B) of 5-dodecyne (**Ia**) and 2.68 mmol (67% yield based on R_3B) of (Z)-5-acetoxy-5-dodecene (**IIa**), along with 0.32 mmol (8% yield based on R_3B) of hexyl ethanoate, were obtained by the reaction of 4 mmol of trihexylborane with 8 mmol of 1-hexyne and 8 mmol of LTA.

Some synthetic methods for the internal enol acetate have hitherto been reported.[6] However, the present reaction has following features. One of alkyl groups of trialkylborane adds to the terminal carbon of the acetylenic triple bond, and the acetoxy group to its internal position respectively. Accordingly, the unsaturated bond of 1-alkyne remains as a double bond in the enol acetate. Therefore, one can design the position of the double bond of the internal enol acetate by the choice of alkyne and trialkylborane. An additional important feature is that the all enols formed in this reaction have the Z-configuration. These facts strongly emphasize the synthetic utility of the present reaction.

The following reaction procedure is representative. A dry, 200-ml round bottomed flask, equipped with a gas inlet, a magnetic stirring bar, a septum inlet, a reflux condenser, and a dropping funnel, was flushed with argon. In the flask cyclopentene (5.28 ml, 60 mmol) was hydroborated with 20 mmol of borane in tetrahydrofuran,[7] and then tetrahydrofuran was removed under reduced pressure at room temperature. After the addition of 1-hexyne(4.57 ml, 40 mmol) and hexane(60 ml) to the neat tricyclopentylborane, LTA(17.7 g, 40 mmol) was added to the solution under weak stream of argon. And then the content was stirred at 60°C for 36 hr in suspension. After addition of 20 ml of water at room temperature, the reaction mixture was extracted three times with hexane and benzene. The combined organic layer was washed twice with saturated aqueous sodium chloride solution, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the reaction products were isolated by column chromatography (silica gel, 150 g). On elution with hexane (200 ml), hexane (200 ml) – benzene (200 ml), and benzene (200 ml), 0.93 g (6.20 mmol, 31% based on R_3B) of 1-cyclopentyl-1-hexyne (**Ib**) and 3.73 g (17.8 mmol, 89% based on R_3B) of 2-acetoxy-1-cyclopentyl-1-hexene (Z, > 99%) (**IIb**) were obtained respectively.

The configurations of the enol acetates were assigned by comparison of the vinyl proton chemical shifts with those reported for the enol acetates.[8]

Analitical data of the products are as follows. **Ia**: n_D^{20} 1.4419; MS m/e 166 (M^+); PMR(CCl_4, TMS) δ 0.90(t, 6H), 1.10~1.60(12H), 2.08(t, 4H). **Ib**: n_D^{20} 1.4670; MS m/e 150 (M^+); PMR(CCl_4, TMS) δ 0.89(t, 3H). 1-Phenyl-1-octyne (**Ic**): n_D^{20} 1.5269; MS m/e 186 (M^+-28); IR(neat) 2230 cm^{-1}(-C≡C-, w);[5c] PMR(CCl_4, TMS) δ 0.89(t, 3H), 1.10~1.80(m, 8H), 2.32(t, 2H), 7.19(m, 5H).[5c] (Z)-**IIa**: n_D^{20} 1.4402; MS m/e 226 (M^+); IR(neat) 1760 (C=O, s), 1699 cm^{-1}(C=C);[8a,c] PMR(C_6H_6, TMS) δ 1.80(s, 3H), 4.86(t, 1H, J=7Hz, long-range coupling,~1Hz).[8] (Z)-**IIb**: n_D^{20} 1.4601; MS m/e 210 (M^+); IR(neat) 1765(C=O, s), 1700 cm^{-1}(C=C);[8a,c] PMR(C_6H_6, TMS) δ 1.87(s, 3H) 4.81(dt, 1H, J=8 and~1Hz).[8] (Z)-1-Acetoxy-1-phenyl-1-octene (**IIc**): n_D^{20} 1.5130; MS m/e 246 (M^+-28); IR(neat) 1765 cm^{-1}(C=O, s);[8a,c] PMR(C_6H_6, TMS) δ 1.86(s, 3H), 5.62(t, 1H, J= 7 Hz).[8] 5-tetradecyne (**Id**): n_D^{20} 1.4475; MS m/e 194(M^+); PMR(CCl_4, TMS) δ 0.88(t, 3H), 0.86(t, 3H), 1.10~1.70 (16H), 2.06(t, 4H). (Z)-5-Acetoxy-5-tetradecene (**IId**): n_D^{20} 1.4438; MS m/e 254(M^+); IR (neat) 1760(C=O, s), 1700 cm^{-1}(C=C);[5c] PMR(C_6H_6, TMS) δ 1.79(s, 3H), 4.87(t, 1H, J= 7 Hz, long-range coupling,~1 Hz).[8] 1-Phenyl-1-hexyne (**Ie**): n_D^{20} 1.5382; MS m/e 158(M^+); IR(neat) 2210 cm^{-1}(-C≡C-, w);[5c] PMR(C_6H_6, TMS) δ 0.92(t, 3H), 1.10~1.80(m, 4H), 2.33 (t, 2H), 7.17(m, 5H).[5c] (Z)-1-Acetoxy-1-phenyl-1-hexene (**IIe**): n_D^{20} 1.5223; MS m/e 218 (M^+); IR(neat) 1765 cm^{-1}(C=O, s);[8a,c] PMR(C_6H_6, TMS) δ 1.87(s, 3H), 5.61(t, 1H, J=7 Hz).[8]

References and Notes

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