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TRIALKYLBORANE-INDUCED CHLORINATIONS OF ALKANE WITH CHLORINE, t-BUTYL HYPOCHLORITE AND N-CHLOROSUCCINIMIDE

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Trialkylboranes initiated the chlorinations of alkanes with radical chlorinating agents such as chlorine, t-butyl hypochlorite and N-chlorosuccinimide. The reactions proceeded at 20 °C even in the dark giving monochloroalkanes.

Previously the authors reported that trialkylboranes initiated the chlorination of alkanes with iodobenzene dichloride.[1)] The observed highly selective introduction of a chlorine atom on an internal carbon atom of the alkanes suggests that the iodobenzene chloride radical, $\mathrm{Ph\dot{I}Cl}$, is involved in the reaction as in the photoinduced reaction with the same reagent,[2,3)] and thus trialkylborane acts as an initiator of the reaction. None of other types of organometallic compounds such as alkoxydialkylborane, dialkoxyalkylborane, trialkylaluminium and alkyllithium showed such a remarkable initiating property as trialkylborane. Although the recent progress in the chemistry of organoborane is remarkable, trialkylborane seems to have been utilized mostly as an intermediate in organic syntheses. We were interested in the above facts and examined the initiating property of trialkylborane for the chlorinations of alkanes with some radical chlorinating agents other than iodobenzene dichloride. In this report, trialkylborane-induced chlorinations of alkanes with chlorine, t-butyl hypochlorite and N-chlorosuccinimide are described.

$$\mathrm{PhICl_2} \xrightarrow{\mathrm{R'_3B}} \mathrm{Ph\dot{I}Cl} + \mathrm{Cl\cdot}$$
$$\mathrm{Ph\dot{I}Cl} + \mathrm{RH} \longrightarrow \mathrm{R\cdot} + \mathrm{PhI} + \mathrm{HCl}$$
$$\mathrm{R\cdot} + \mathrm{PhICl_2} \longrightarrow \mathrm{RCl} + \mathrm{Ph\dot{I}Cl}$$

All reactions were carried out by using 60 mmol of alkanes and 6 mmol of chlorinating agents at 20 °C and the results are shown in Table 1.

In the presence of trihexylborane, chlorine dissolved in carbon tetrachloride chlorinated 2,3-dimethylbutane in the dark giving a mixture of 1-chloro-2,3-dimethylbutane and 2-chloro-2,3-dimethylbutane. Although a part of hexyl group of trialkylborane was converted to chlorohexane, the most of chlorine was utilized for the chlorination of 2,3-dimethylbutane. When a small amount of trihexylborane, 0.3-0.9 mmol, was employed, chlorine seemed to be consumed almost exclusively for the chlorination of 2,3-dimethylbutane. The reaction proceeded rapidly at 20 °C, and gave a fairly good yield of chloro-2,3-

dimethylbutanes in 1 h, in contrast to the poor yield obtained in the absence of trihexylborane under the same reaction conditions.

The reaction was not regioselective. No remarkable change was observed in the distribution of chloro-2,3-dimethylbutane isomers when trialkylborane was changed from trihexylborane to tributylborane or tricyclohexylborane. Further, as appeared in the chlorination with iodobenzene dichloride, the yield and the isomer distribution were similar to those obtained in the photoinduced chlorination with the same reagent. Accordingly, trialkylborane seems to act as an initiator of the reaction which gives the chlorine radical.

Similar results were obtained when 3-methylpentane or n-heptane was subjected to the reaction.

t-Butyl hypochlorite was known to chlorinate 2,3-dimethylbutane in the presence of 2,2'-azobis(2-methylpropionitrile) or under the irradiation of light to give 2-chloro-2,3-dimethylbutane as the main reaction product.4) Likewise, in the presence of trihexylborane, this reagent chlorinated 2,3-dimethylbutane in the dark at 20 °C giving 2-chloro-2,3-dimethylbutane as the main product accompanied by the small amount of 1-chloro-2,3-dimethylbutane. It was reported that in the reaction of a deficient amount of t-butyl hypochlorite with a mixture of trialkylborane and cyclopentane, chloroalkane and chlorocyclopentane were formed competitively.5) However, in the present reaction, the presence of 0.3 mmol of trihexylborane was found to initiate the effective chlorination of 2,3-dimethylbutane without the formation of any detectable amount of chlorohexane derived from trihexylborane. Similar results were obtained when 3-methylpentane and n-heptane were subjected to the reaction.

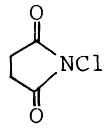
It has been reported that in the presence of benzoyl peroxide, N-chlorosuccinimide chlorinated alkanes on refluxing for 12 h in carbon tetrachloride giving chloroalkanes in moderate yield.6)

In the presence of 0.3 mmol of trihexylborane, chlorination of alkanes with N-chlorosuccinimide was so sluggish that only a trace amount of chloroalkane was formed after 24 h of the reaction at 20 °C. However, the yield of chloroalkanes increased with the increase of the quantity of trihexylborane. For example, with 1.5 mmol of trihexylborane, 2,3-dimethylbutane gave a 56% yield of a mixture of 1-chloro-2,3-dimethylbutane and 2-chloro-2,3-dimethylbutane (1 : 99) at 20 °C even in the dark. Like other cases described above, the presence of large amount of trihexylborane reduced the yield of the desired chloroalkanes and increased the amount of chlorohexane. While, the photoinduced chlorination, carried out under the same reaction conditions, gave no reaction product.

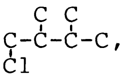
There have been some controversies about the radical chain carrier of the chlorination of alkanes with N-chlorosuccinimide.7—9) In contrast to the chlorination with chlorine, the high regioselectivity shown in this reaction seems to suggest that the radical chain carrier is not the chlorine atom but succinimide radical.

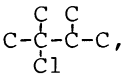
In above three chlorinations trialkylborane seems to initiate the chlorination in a similar manner, and the reaction mechanisms may roughly been

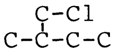
Table 1. Chlorinations of Alkanes with Chlorine, t-Butylhypochlorite and N-Chlorosuccinimide in the Presence of Trialkylborane.[a]

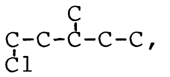
Chlorinating agent	Alkane	Initiator	Reaction time /h	Product[b] (Yield /%)[c]		
Cl_2	2,3-Dimethylbutane	$(n\text{-}C_4H_9)_3B$	1	A (47)	B (35)	
		$(n\text{-}C_6H_{13})_3B$	1	A (46)	B (35)	
		$(c\text{-}C_6H_{11})_3B$	1	A (47)	B (33)	
		Light[d]	1	A (43)	B (28)	
	3-Methylpentane	$(n\text{-}C_6H_{13})_3B$	1	C (35)	D (41)	E (13)
	n-Heptane	$(n\text{-}C_6H_{13})_3B$	1	F (15)	G (75)	
t-BuOCl	2,3-Dimethylbutane	$(n\text{-}C_4H_9)_3B$	1	A (9)	B (80)	
		$(n\text{-}C_6H_{13})_3B$	1	A (13)	B (84)	
		$(c\text{-}C_6H_{11})_3B$	1	A (27)	B (56)	
		Light[d]	1	A (11)	B (76)	
	3-Methylpentane	$(n\text{-}C_6H_{13})_3B$	1	C (14)	D (40)	E (31)
	n-Heptane	$(n\text{-}C_6H_{13})_3B$	1	F (6)	G (86)	
	2,3-Dimethylbutane	$(n\text{-}C_4H_9)_3B$	24	A (0.6)	B (63)	
		$(n\text{-}C_6H_{13})_3B$	24	A (0.6)	B (55)	
		$(c\text{-}C_6H_{11})_3B$	24	A (1.5)	B (48)	
		Light[d]	24	None		
	3-Methylpentane	$(n\text{-}C_6H_{13})_3B$	24	C (1)	D (31)	E (19)
	n-Heptane	$(n\text{-}C_6H_{13})_3B$	24	F (0.5)	G (50)	

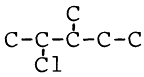
a) The reaction was carried out at 20 °C by using 60 mmol of alkane and 6 mmol of chlorinating agent, and 0.3 mmol of trialkylborane except for the reaction with N-chlorosuccinimide where 1.5 mmol of trialkylborane was used. b) Reaction products are represented as follows for convenience:

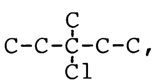

$\underset{Cl}{C}-\overset{C}{C}-\overset{C}{C}-C$, A;

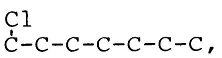

$C-\underset{Cl}{\overset{C}{C}}-\overset{C}{C}-C$, B;

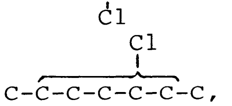

$C-\overset{C-Cl}{C}-C-C$ and


$\underset{Cl}{C}-C-\overset{C}{C}-C-C$, C;


$C-\underset{Cl}{C}-\overset{C}{C}-C-C$, D;


$C-C-\underset{Cl}{\overset{C}{C}}-C-C$, E;


$\overset{Cl}{C}-C-C-C-C-C-C$, F;

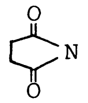

$C-\overbrace{C-C-C-C-C}^{Cl}-C$, G

c) Estimated by GLC and based on the chlorinating agent employed. d) A 500-W high pressure mercury lamp was used.

written as follows.

$$\begin{array}{l} XCl \xrightarrow{R'_3B} X\cdot + Cl\cdot \\ X\cdot + RH \longrightarrow R\cdot + XH \\ R\cdot + XCl \longrightarrow RCl + X\cdot \end{array}$$

X = Cl, t-BuO,



However, in the reactions with t-butyl hypochlorite and N-chlorosuccinimide a small but apparent effect of the structure of alkyl group of trialkylborane upon the isomer distribution was observed in contrast to the reaction with chlorine. Thus, in the case of tributylborane, the ratio of the terminal chloroalkane increased compared with that in the case of tricyclohexylborane. On the other hand, the situation was reversed in the case of tricyclohexylborane. Accordingly further studies must be needed to clarify the role of trialkylborane and the mechanisms of these reactions. The detailed study and the utilization of this effect will be appeared elsewhere.

The following experimental procedure is representative. In a 50-ml round bottomed flask, protected from light by black plastic bag and flushed with argon, 60 mmol of 2,3-dimethylbutane and 0.3 mmol of trihexylborane[10)] were placed. To the stirred solution 6 mmol of chlorine in 6 ml of carbon tetrachloride was slowly added at 20 °C. After 1 h of the reaction under the weak stream of argon, the reaction mixture was neutralized with aqueous sodium hydroxide and washed several times with NaCl-saturated water. The reaction mixture was analysed by GLC using chlorobenzene as an internal standard material. In the reaction using t-butyl hypochlorite, the experimental procedure was the same as described above. The reaction with N-chlorosuccinimide was carried out in a similar manner as described in our previous paper.[1)]

References

1) A. Arase, M. Hoshi, and Y. Masuda, Chem. Lett., 1979, 961.
2) D. F. Banks, E. S. Huyser, and J. Kleinberg, J. Org. Chem., 29, 3962 (1964).
3) D. D. Tanner and P. B. VanBoster, J. Org. Chem., 32, 1511 (1967).
4) C. W. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6108 (1960).
5) A. G. Davies, T. Maki, and B. P. Roberts, J. Chem. Soc., Perkin Trans. 1, 1972, 744.
6) N. P. Buu-Hoi and P. Demerseman, J. Org. Chem., 18, 649 (1953).
7) G. F. Bloomfield, J. Chem. Soc., 1944, 114.
8) J. Adam, P. A. Gosselain, and P. Goldfinger, Nature, 171, 704 (1953).
9) T. Migita, M. Nakayama, T. Watanuki, M. Suzuki, and M. Kosugi, Bull. Chem. Soc. Jpn., 54, 822 (1981).
10) Trihexylborane was prepared by hydroboration of 1-hexene with BH_3 in THF and used after the removal of THF under the reduced pressure.

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