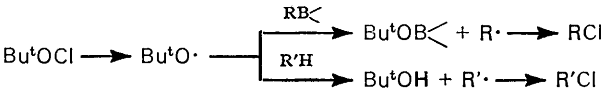
Homolytic Organometallic Reactions. Part VI.[1] The Reaction of t-Butyl Hypochlorite with Organoboranes. Rate Constants for Bimolecular t-Butoxydealkylation at Boron

By **Alwyn G. Davies,* Takao Maki, and B. P. Roberts**, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

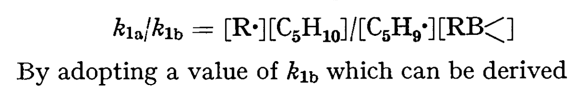
t-Butyl hypochlorite reacts with organoboranes by a process involving bimolecular homolytic t-butoxydealkylation at boron [equation (i)]. The kinetic parameters for these processes have been determined by causing the organoboranes to compete with cyclopentane or cyclohexane for reaction with the t-butoxyl radicals [equation (ii)], and analysing the relative yields of the two alkyl chlorides by g.l.c.



$$\mathrm{Bu^tOCl} \longrightarrow \mathrm{Bu^tO\cdot} \begin{cases} \xrightarrow{\mathrm{RB}<} \mathrm{Bu^tOB}< + \mathrm{R\cdot} \longrightarrow \mathrm{RCl} & \text{(i)} \\ \xrightarrow{\mathrm{R'H}} \mathrm{Bu^tOH} + \mathrm{R'\cdot} \longrightarrow \mathrm{R'Cl} & \text{(ii)} \end{cases}$$

This confirms and extends the results which have been obtained previously by an e.s.r. method.

In Part III [2] it was shown that, if di-t-butyl peroxide was photolysed in the presence of alkylboranes, the t-butoxyl radicals which are formed bring about an S_H2 reaction at the boron centre, and the displaced alkyl radicals can be observed by e.s.r. spectroscopy. Rate constants for this process were determined by causing cyclopentane to compete with the alkylborane for reaction with the t-butoxyl radicals [equation (1)]. If it can be assumed that the rate constants describing the removal of the alkyl radical R· and the cyclopentyl radical $C_5H_9\cdot$ from the system are equal,[3] then the ratio of the rate constants for the two reactions is given by equation (2).



$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} 2\mathrm{Bu^tO\cdot} \begin{cases} \xrightarrow[\mathrm{a}]{\mathrm{RB}<} \mathrm{Bu^tOB}< + \mathrm{R\cdot} \\ \xrightarrow[\mathrm{b}]{\mathrm{C_5H_{10}}} \mathrm{Bu^tOH} + \mathrm{C_5H_9\cdot} \end{cases} \qquad (1)$$

$$k_{1a}/k_{1b} = [\mathrm{R\cdot}][\mathrm{C_5H_{10}}]/[\mathrm{C_5H_9\cdot}][\mathrm{RB}<] \qquad (2)$$

By adopting a value of k_{1b} which can be derived from the literature, an internally consistent set of absolute

---

[1] Part V, A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1971, 2171.

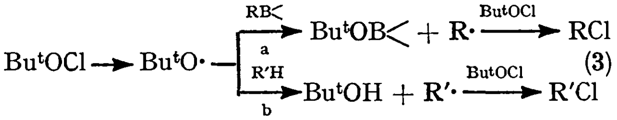
[2] Part III, A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1823.

[3] D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7047; D. J. Carlsson, K. U. Ingold, and L. C. Bray, *Internat. J. Chem. Kinetics*, 1969, **1**, 315.

rate constants, k_{1a}, for a series of alkylboranes was obtained.

This paper described an alternative method, based on the reaction of t-butyl hypochlorite with organoboranes,[4] by which the ratio k_{1a}/k_{1b} can be determined, and which avoids any assumption about the rates of removal of radicals. It proves a check on our first method, and can be applied to some organoboranes which could not be handled by the e.s.r. technique.

Tudor has shown that alkyl hypochlorites react with organoboranes to give alkylboranes and alkyl chlorides, RCl, by a chain reaction involving homolytic alkoxydealkylation at the boron centre [reaction (3a)].[4] If a hydrocarbon (R'H) is present, this will compete with the organoborane for reaction with the alkoxyl radical, leading to the formation of the alkyl chloride, R'Cl [reaction (3b)]. If the products are analysed for the two alkyl chlorides, the ratio k_{3a}/k_{3b} will be given by equation (4), providing both the borane and hydrocarbon are present in excess with respect to the hypochlorite, and if the value of k_{3b} is known, the absolute value of k_{3a} can be derived.



$$\mathrm{Bu^tOCl} \longrightarrow \mathrm{Bu^tO}\cdot \begin{cases} \xrightarrow[\mathrm{a}]{\mathrm{RB}<} \mathrm{Bu^tOB}< + \mathrm{R}\cdot \xrightarrow{\mathrm{Bu^tOCl}} \mathrm{RCl} \\ \xrightarrow[\mathrm{b}]{\mathrm{R'H}} \mathrm{Bu^tOH} + \mathrm{R'}\cdot \xrightarrow{\mathrm{Bu^tOCl}} \mathrm{R'Cl} \end{cases} \qquad (3)$$

$$\frac{k_{3a}}{k_{3b}} = \frac{\log\,[\mathrm{RB}<]_\infty/[\mathrm{RB}<]_0}{\log\,[\mathrm{R'H}]_\infty/[\mathrm{R'H}]_0} \qquad (4)$$

The subscripts $_0$ and $_\infty$ refer to the beginning and end of reaction. If both substrates are present in large excess with respect to the hypochlorite (as was usual in in our experiments), we may use the relation $k_{3a}/k_{3b} = [\mathrm{RCl}][\mathrm{R'H}]/[\mathrm{R'Cl}][\mathrm{RB}<]$.

EXPERIMENTAL

Many of the experimental methods have been described in earlier Parts of this series.[1,2] Trineopentylborane was prepared from neopentylmagnesium chloride and boron trifluoride.[5] t-Butyl hypochlorite was obtained from t-butyl alcohol and sodium hypochlorite,[6] and was stored in a refrigerator: small batches of the reagent were prepared frequently, because it decomposes with time. Trichloroethylene was washed with water, dried ($CaCl_2$), and distilled before use.

Initiation.—Throughout these experiments, di-t-butyl hyponitrite (1% with respect to t-butyl hypochlorite) was used as an initiator.[7] At 0° the reactions were initiated photolytically with a 40-W tungsten filament lamp placed 5 cm from the reaction vessel.

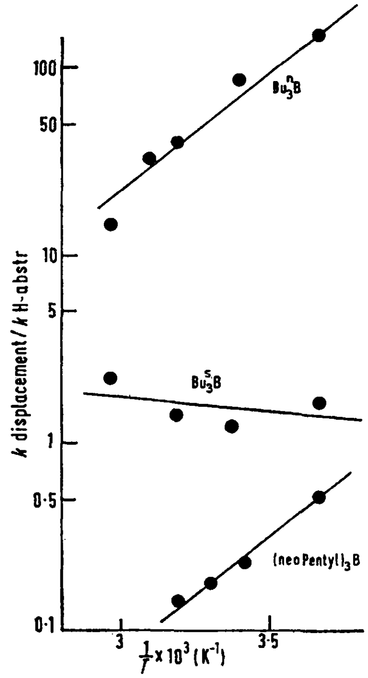
Apparatus and Procedure.—All reactions were carried out in a flat-bottomed creased glass flask (*ca.* 10 ml), carrying a magnetic stirrer and sealed with a serum cap. The flask was immersed in a thermostatted bath controlled by contact-thermometer.

All the reactants except the borane, hypochlorite, and initiator were weighed into the reaction vessel, and degassed by freeze-thaw cycles. The borane was then added by syringe through the serum cap, and when the temperature was steady, the hypochlorite and initiator solution were added with continuous stirring to avoid local reaction. All the hypochlorite was usually consumed within 1 h.

Product Analysis.—Products were analysed by gas-liquid chromatography on a 2-m column of Apiezon-L (15%) on Chromosorb P, using chlorobenzene as an internal standard. The temperature was programmed from 60 to 110°.

RESULTS AND DISCUSSION

t-Butyl hypochlorite was caused to react with a series of organoboranes in the presence of cyclohexane, cyclopentane, or 2,3-dimethylbutane, over the temperature range 0—65°. Trichloroethylene was added to suppress any propagation by chlorine radicals.[8] The yields of the two alkyl chlorides which were formed according to equation (3) were determined by gas-liquid chromatography. Relative values of the rate constants for the two reactions were derived by equation (4), and put on an absolute basis by adopting values of k_{3b} for cyclohexane of $1{\cdot}2 \times 10^9 \exp(-5{\cdot}20/RT)$ and for cyclopentane of $1{\cdot}0 \times 10^9 \exp(-5{\cdot}20/RT)$ where RT is in kcal mol^{-1}.[2] The results are shown in Tables 1—3, and in the Figure.



Temperature dependence of ratio of rate constants

Tri-n-butylborane reacted cleanly with t-butyl hypochlorite, and gave a good chlorine balance according to equation (3), and only a trace of acetone could be detected. To check that the chain-carrying species was $\mathrm{Bu^tO}\cdot$ and not $\mathrm{Cl}\cdot$, the reaction was carried out in the

---

[4] A. G. Davies, D. Griller, B. P. Roberts, and R. Tudor, *Chem. Comm.*, 1970, 640.

[5] F. M. Rossi, P. A. McCusker, and G. F. Hennion, *J. Org. Chem.*, 1967, **32**, 1233.

[6] M. J. Mintz and C. Walling, *Org. Synth.*, 1969, **49**, 9.

[7] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 1966, 6163.

[8] C. Walling and J. A. McGuinness, *J. Amer. Chem. Soc.*, 1969, **91**, 2053.

presence of 2,3-dimethylbutane, for which the relative reactivities of the hydrogen bonded to the tertiary and primary centres are known.[9] The relative yields of the chlorides $Me_2CH{\cdot}CMe_2Cl$ and $Me_2CH{\cdot}CHMe{\cdot}CH_2Cl$ showed that this ratio was 43·3 : 1 (per C–H bond), which agrees with the selectivity of the t-butoxyl radical (45 : 1), but not that for the chlorine atom (4 : 1). If a small amount of hydrogen chloride was added to the reaction involving tri-n-butylborane and cyclohexane, the ratio of n-butyl chloride:cyclohexyl chloride in the product was reduced, presumably because of the incursion of a chlorine-chain reaction. We believe then that, under our normal conditions, the t-butoxyl radical is the chain-carrying species.

Tri-n-butylborane in competition with cyclohexane gave a satisfactory Arrhenius plot (Figure), but the apparent rate constants were less by a factor of *ca.* 4 than those obtained by the e.s.r. method. This difference is due to different *A*-factors obtained by the two methods, but, in view of probable experimental errors which are involved, the agreement between the results obtained by the two independent techniques is satisfactory.

TABLE 1

Rate constants for homolytic t-butoxydealkylation at 40°

		Initial concentration (M)						Chlorine Balance		
R_3B	R′H	R_3B	R′H	Bu^tOCl	$CHCl{=}CCl_2$	Solvent	Others	(%)	k_{3a}/k_{3b}	k_{3a} ($l\ mol^{-1}\ s^{-1}$) [a]
$Bu^n{}_3B$	C_6H_{12}	0·683	7·33	0·108	0·187			94·3	38·5	1×10^7 [c]
$Bu^n{}_3B$	2,3-Dimethylbutane	1·08	5·33	0·121	0·145			87·9	33·3	5×10^6 [c]
$Bu^i{}_3B$	C_6H_{12}	0·898	7·29	0·123	0·153			89·8	1·30	3×10^5 [d]
$Bu^i{}_3B$	C_5H_{10}	1·43	5·44	0·229	0·889			96·7	1·05	2×10^5 [d]
$Bu^i{}_3B$	C_5H_{10}	0·271	9·37	0·118				93·4	1·25	3×10^5 [d]
$Bu^s{}_3B$	C_6H_{12}	2·08	4·17	0·105	0·136			38·1	1·41	4×10^5 [e]
$(Bu^nBO)_3$	C_6H_{12}	1·16	5·50	0·139	0·158			72·5	3·65	1×10^6 [f]
$(PhCH_2)_3B$	C_6H_{12}	0·301		0·0363	0·0444	$C_2F_3Cl_3$	$Bu^n{}_3B$	40·7	2·87 [b]	3×10^7
$Pe^{neo}{}_3B$	C_6H_{12}	0·308	1·54	0·0560	0·259	$C_2F_3Cl_3$		98·4	0·140	4×10^4

[a] Taking $k_{3b}(C_6H_{12}) = 2{\cdot}6 \times 10^5\ l\ mol^{-1}\ s^{-1}$; $k_{3b}(C_5H_{10}) = 2{\cdot}2 \times 10^5\ l\ mol^{-1}\ s^{-1}$; k_{3b}(2,3-Dimethylbutane) $= 1{\cdot}4 \times 10^5\ l\ mol^{-1}\ s^{-1}$ (P. Wagner and C. Walling, *J. Amer. Chem. Soc.*, 1965, **87**, 5179). [b] $k_{3a}(Benzyl_3B)/k_{3a}(Bu_3B)$. Values of k_{3a} at 40° obtained by the e.s.r. method: [c] 3×10^7; [d] 1×10^6; [e] 3×10^5; [f] $6 \times 10^5\ l\ mol^{-1}\ s^{-1}$.

TABLE 2

Temperature dependence of k_{3a}/k_{3b}

		Initial concentration (M)				
R_3B	Temp.	R_3B	C_6H_{12}	Bu^tOCl	$CHCl{=}CCl_2$	k_{3a}/k_{3b}
$Bu^n{}_3B$	65°	1·17	6·27	0·115	0·146	14·2
$Bu^n{}_3B$	50	1·19	6·20	0·114	0·133	32·5
$Bu^n{}_3B$	40	0·683	7·33	0·108	0·187	38·5
$Bu^n{}_3B$	21	1·11	6·37	0·107	0·135	82·2
$Bu^n{}_3B$	0	1·27	6·04	0·114	0·142	146
$Bu^s{}_3B$	65	2·15	4·03	0·107	0·137	2·21
$Bu^s{}_3B$	40	2·08	4·17	0·105	0·136	1·41
$Bu^s{}_3B$	23	2·07	4·18	0·121	0·134	1·20
$Bu^s{}_3B$	0	2·00	4·37	0·112	0·134	1·63
$Pe^{neo}{}_3B$ [a]	40	0·308	1·54	0·0560	0·259	0·140
$Pe^{neo}{}_3B$ [a]	30	0·353	1·59	0·0612	0·0662	0·185
$Pe^{neo}{}_3B$ [a]	20	0·369	1·47	0·0608	0·0753	0·233
$Pe^{neo}{}_3B$ [a]	0	0·368	1·46	0·0613	0·0652	0·518

[a] Solvent $C_2F_3Cl_3$.

TABLE 3

Activation parameters for homolytic alkoxydealkylation

Reactant	*E* (kcal mol^{-1})	*A* ($l\ mol^{-1}\ s^{-1}$)
$Bu^n{}_3B$	−0·3 [a]	$6{\cdot}1 \times 10^6$ [c]
$Bu^s{}_3B$	5·9 [b]	$5{\cdot}1 \times 10^9$ [d]
$Pe^{neo}{}_3B$	0·7	$1{\cdot}1 \times 10^5$
C_6H_{12}	5·2	$1{\cdot}2 \times 10^9$

By the e.s.r. method: [a] 0, [b] 4·5 kcal mol^{-1}, [c] $3{\cdot}5 \times 10^7$, [d] $4{\cdot}9 \times 10^8\ l\ mol^{-1}\ s^{-1}$.

With tri-isobutylborane, competition reactions were carried out with both cyclohexane and cyclopentane. Again, the chlorine balance according to equation (3) was good. Consistent results were obtained, but again the rate constants were *ca.* four times less than those obtained by our former method. Omission of trichloroethylene from the system appeared to have no effect; cyclohexene was also tried as a trap for chlorine atoms, but it underwent allylic chlorination.

Tri-n-butylboroxine showed a rate constant which was rather higher than that which we obtained previously, but the values obtained for tri-s-butylborane at 40° by the two methods were in good agreement. With tri-s-butylborane, the chlorine balance was low, perhaps because some abstraction occurred of the hydrogen bonded to the secondary carbon atom.

$$(MeEtCH)_3B \xrightarrow{Bu^tO\cdot} MeEt\dot{C}B(CHMeEt)_2 \xrightarrow{Bu^tOCl} (MeEtCCl)B(CHMeEt)_2 \quad (5)$$

The ready abstraction of hydrogen from the αC–H bond in a trialkylborane by halogen atoms is a well established reaction.[10]

Tribenzylborane might be expected to show a high reactivity because the displaced benzyl radical would be resonance-stabilised. Our attempts to determine the reactivity by the e.s.r. method were unsuccessful because of the poor signal to noise ratio in the spectra obtained, but a satisfactory result has been obtained by the present method, by causing tribenzylborane and tri-n-butylborane to compete for t-butyl hypochlorite. A considerable amount of t-butyl alcohol was formed, and the chlorine balance on the basis of reaction (3) was low,

---

[9] G. A. Russell, *J. Amer. Chem. Soc.*, 1958, **80**, 4987.

[10] J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Organometallic Chem.*, 1969, **19**, 431; C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, 1970, **92**, 7212.

because t-butoxyl radicals abstracted benzylic hydrogen atoms. Towards the S_H2 attack by the t-butoxyl radical at boron, tribenzylborane was found to be only 2·9 times as reactive as tributylborane at 40°. This low selectivity is probably a consequence of the very high reactivity. Alkoxydealkylation at boron in trialkylboranes is always a very exothermic process with a low activation energy. The transition state is therefore reached only a short distance along the reaction co-ordinate, and resembles the reactants rather than the products, with very little stretching of the boron–carbon bond. Benzylic resonance in the incipient benzyl radical is therefore little developed, and can have little stabilising effect. Similarly in the autoxidation of tribenzylborane it has been found that the rate constant for displacement of a benzyl radical by the benzylperoxyl radical is only slightly greater than that for butylperoxydealkylation of tri-n-butylborane.[11]

The reaction of trineopentylborane [5] was examined in an attempt to identify a steric effect on the reactivity. At 40°, the rate constant for the S_H2 process was about one three hundredth of that for tri-n-butylborane, but this was due principally to a lower A factor rather than to a significantly higher activation energy. It appears that the bulky neopentyl groups impose a high degree of order on the transition state without contributing appreciably to the activation energy.

Conclusion.—The differences between the two methods which have now been used for determining the rate constants for the S_H2 t-butoxydealkylation at boron are substantial. The e.s.r. method involves generation of t-butoxyl radicals by photolysis of di-t-butyl peroxide, measures relative concentrations of alkyl radical intermediates in a non-chain process, and makes an assumption about the rate constants for the removal of these radicals.* The method described here obtains the t-butoxyl radical from a thermal chain reaction of t-butyl hypochlorite, measures the concentration of products of the reaction by g.l.c., and does not involve the assumption mentioned above. Yet the two different methods have given results which differ, at the most, by a factor of 4. We think that this vindicates the e.s.r. technique, and indicates that it can be applied to the study of a wide range of homolytic reactions.

We are grateful to Mitsubishi Chemical Industries Ltd. for financial support of (T. M.), and to Mr. K. G. Foot for the gift of trineopentylborane. This work was carried out during the tenure of a Turner and Newall Research Fellowship (by B. P. R.).

[1/1847 *Received, October* 11*th*, 1971]

---

* It is possible that the anomalous intensities which are sometimes observed [12–14] in the e.s.r. spectra of short lived radicals could lead to a false estimate od radical concentrations. In kinetic experiments where photolytically generated radicals have been studied by e.s.r., we have never observed anomalous intensity distribution among hyperfine components (e.s.r. multiplet effect). It seems doubtful that a net polarisation effect could complicate our radical concentration measurements without the existence of a multiplet effect, and we believe that the agreement between the kinetic e.s.r. results and those presented in this paper serves to prove that such effects are unimportant in the former method.

[11] S. Korcek, G. B. Watts, and K. U. Ingold, *J.C.S. Perkin II*, 1972, 242.

[12] H. Zeldes and R. Livingston, *J. Phys. Chem.*, 1970, **74**, 3336.

[13] P. Neta, R. W. Fessenden, and R. H. Schuler, *J. Phys. Chem.*, 1971, **75**, 1654.

[14] F. J. Adrian, *J. Chem. Phys.*, 1971, **54**, 3918.