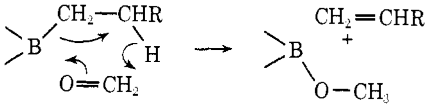
(7)

Tri-*n*-octylborane reacts similarly, producing 85% of 1-octene in the absence of air. In the presence of air 79% of the homologated alcohol was obtained (with 10% 1-octene).

In the absence of air triisobutylborane (10 mmol) reacts within 1 hr. Oxidation produced 20 mmol of isobutyl alcohol and no homologated alcohol. Consequently, one alkyl group had been eliminated by the formaldehyde. In the presence of air, the homologated product (29%) was formed.

Tri-*sec*-butylborane reacts only slowly at 0° in the absence of air. In the presence of 5 mol % of iodine, no borane was observed to react over a 4-hr period. Presumably the borane is sufficiently hindered so as to resist formation of the cyclic transition state. At a higher temperature, 120° in diglyme, a facile dealkylation takes place to give methyl di-*n*-butylborinate. At 0°, air induces the chain reaction, providing the homologated product, 2-methyl-1-butanol (45%).

Thus primary alkylboranes react quite readily through the nonradical path, while the more hindered secondary alkylboranes react only sluggishly. The straight-chain boranes also react readily by the free-radical path, but branching in the alkyl group reduces the yield of the homologated product.

Carbonylation of 9-alkyl-9-borabicyclononane reagents provides an efficient general route for the one-carbon homologation of olefins.[13] Consequently, the formaldehyde reaction is primarily of theoretical interest. It is the first example of a direct addition of an organoborane to a carbonyl group. Moreover, it is of interest that the reaction with monomeric formaldehyde can be directed to either the free-radical or nonradical mechanism. This suggests that other reactions of organoboranes may be controlled to follow both radical and nonradical pathways. We are continuing to explore these possibilities.

(13) H. C. Brown, E. F. Knights, and R. A. Coleman, *J. Amer. Chem. Soc.*, **91**, 2144 (1969).

(14) National Science Foundation Predoctoral Fellow, 1970–1972.

(15) Graduate research assistant on Grant No. GP 27742X from the National Science Foundation.

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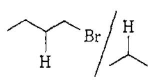
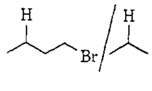
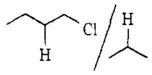
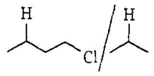
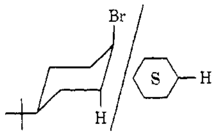
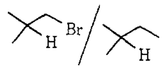
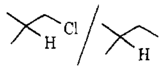
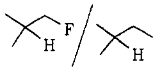
Received May 1, 1972

Anchimeric Assistance in Radical Brominations of Bromoalkanes. Bridged Transition State. Contradiction of Claims by Tanner, *et al.*

Sir:

To obtain further evidence for anchimeric assistance in bromine atom attack on the β hydrogens of alkyl bromides,[1] a series of competition photobrominations were examined in which the substrates were alkanes and bromoalkanes of similar structure. The reaction system consisted of substrates, *N*-bromosuccinimide (NBS) and bromine in methylene chloride solvent.[2] These solutions were degassed and then irradiated in a constant temperature bath with a tungsten filament lamp. The results of these reactions are shown in Table I.

Table I. Relative Rates of Hydrogen Abstraction by Bromine Atoms

Reactants	T, °C	$(k_X/k_H)_{obsd}$
	60	1.4
	30	2.5
	0	4.1
	−23	7.2
	60	0.35
	30	0.37
	0	0.34
	−23	0.32
	60	0.092
	30	0.25
	30	19.2 (115 per H)[a]
	35	8.0
	35	0.4[b]
	35	0.036[b]

[a] Photobromination of *cis*-4-*tert*-butylcyclohexyl bromide yields *trans*-1,2-dibromo-*cis*-4-*tert*-butylcyclohexane: P. S. Skell and P. D. Readio, *J. Amer. Chem. Soc.*, **86**, 3334 (1964). [b] Unpublished work of D. C. Lewis, this laboratory.

In all of the reactions studied, hydrogen abstraction is faster at a position β to a bromine substituent than for the corresponding alkane. The relative reactivities do not parallel those which would be predicted on the basis of simple inductive theory. Reactivity of hydrogen atoms for a straight chain alkyl bromide would be expected to increase with increasing distance between the electronegative substituent and the site of substitution, finally reaching a value characteristic for alkanes. For example, the 3 position of 1-bromobutane is 0.37 times as reactive as that of an unsubstituted secondary hydrogen of propane. One would predict that the reactivity at the 2 position of 1-bromobutane should be further reduced by a factor of at least $1/2.7 = 0.37$.[3] Thus, the 2 position should be $0.37 \times 0.37 = 0.14$ times as reactive as propane. The observed relative rate (2.5 at 30°) is 18 times what would be expected from inductive effects.

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(1) W. A. Thaler, *J. Amer. Chem. Soc.*, **85**, 2607 (1963).

(2) The reaction between hydrogen bromide and NBS has been found to be rapid and complete under the conditions employed. These results are forthcoming in a full paper on this work.

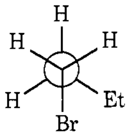
(3) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4231 (1953).

Table II. Photobromination of 1-Bromobutane[a]

Run no.	Temp, °C	C_4H_9Br, mmol	Br, mmol	NBS, mmol	CH_2Cl_2, ml	$C_4H_8Br_2$,[b] mmol	HBr,[c] *M*	1,3/1,2[d]
1	60	18.6	3.1	0	0	3.0	1.5	0.16
2	60	18.6	3.1	0	0	0.31	0.15	0.29
3	60	18.6	0.31	0	0	0.31	0.15	0.15
4	60	18.6	3.1	0	0	0.06	0.03	0.15
5	60	18.6	0.09	0	0	0.09	0.045	0.16
6	60	18.6	0.2	0	0	0.195	0.1	0.18
7	60	9.6	1.6	0	10	0.16	0.016	0.22
8	60	4.8	0.8	0	10	0.075	0.10	0.22
9	60	4.8	0.8	0	10	0.72	0.07	0.19
10	60	2.6	0.31	2.0	12	0.30	0	0.24
11	60	2.6	0.31	2.0	12	0.25	0	0.24
12	40	36.5	6.1	0	0	0.034	0.007	0.18
13	32	46.5	0.1	2.0	5	0.10	0	0.15
14	32	46.5	10.0	2.0	5	0.20	0	0.15
15	32	2.6	0.31	2.0	12	0.34	0	0.15
16	30	2.6	0.31	2.0	12	0.32	0	0.15
17	30	2.6	0.31	2.0	12	0.40	0	0.12
18	0	2.6	0.31	2.0	12	0.54	0	0.081
19	0	2.6	0.31	2.0	12	0.48	0	0.086
20	−23	2.6	0.31	2.0	12	0.24	0	0.040
21	−23	2.6	0.31	2.0	12	0.35	0	0.050

[a] Reaction mixtures were degassed and sealed off prior to exposure to a 300-W tungsten filament lamp (Pyrex filter). [b] Relative to 1,3-dibromopropane added as standard (mass balances were typically >95%). [c] Estimated final HBr concentration from product yield. [d] After removal of unreacted bromine and hydrogen bromide (aqueous $NaHSO_3$) samples were dried (Na_2SO_4) and then analyzed by gas chromatography (Perkin-Elmer F-11, 7% SE-30 on 80–100 Gas Chromosorb R–Z, 15 ft × 1/8 in., 85°, 15 psi of He). Retention times for 1,2-dibromobutane and 1,3-dibromobutane are 28 and 32.3 min, respectively. Reactions run in methylene chloride gave a small unidentified peak following 1,3-dibromobutane; this peak was absent in neat reactions and those run in $CFCl_3$.

Stereochemical studies have shown that >90% of hydrogen abstraction β to a bromine substituent occurs through an antiperiplanar transition state.[4] The conformation of 1-bromobutane that would satisfy the stereochemical requirements (trans) is thermodynamically unfavored, I, and therefore comprises only a small percentage of the rotamers. The partial rate for this rotamer is correspondingly larger than the observed rate enhancement of 18.



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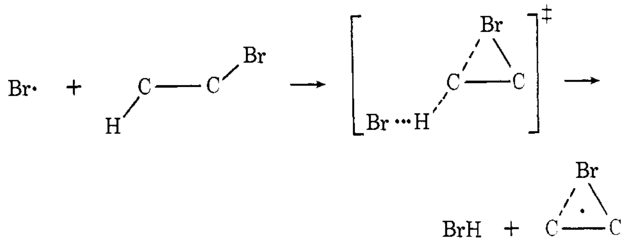
cis-4-*tert*-Butylcyclohexyl bromide, a molecule wherein the geometries of the neighboring bromine substituent and hydrogen atom are fixed in a trans orientation, has ideal geometry for anchimeric assistance. The rate enhancement is the largest observed thus far, 115. If one includes the inductive effect of a β bromine substituent (0.14 times the rate for the alkane) the observed relative rate constant is 820 times the value calculated for unassisted abstraction.

The effect of temperature on the relative rates β and γ to a bromo substituent is unanticipated if bridging does not account for the activation of a β position. The rate of reaction at the γ position of 1-bromobutane changes with temperature almost exactly as the reactivity of propane, indicating nearly identical $\Delta\Delta H^{\ddagger}$ (<100 cal) and $\Delta\Delta S^{\ddagger} = 1$ eu. The values of $\Delta\Delta S^{\ddagger}$ for a range of alkanes reacting with Br falls within 1 eu.[5] By contrast, for (β position of 1-bromobutane) minus propane, $\Delta\Delta H^{\ddagger} = -3.0$ kcal and $\Delta\Delta S^{\ddagger} = -6$ eu.

These observations are consistent with the interpretation of (a) transition state enthalpy lowered by bridging and (b) greater restrictions on the structure of that transition state (more negative $\Delta S^{\ddagger}$), characteristic of the loss of rotational freedom in cyclization processes.



Tanner and coworkers have claimed that anchimeric assistance is an artifact.[6] The only basis for this conclusion is the claim that photobromination of 1-bromobutane in the presence of modest amounts of hydrogen bromide produces 1,3-dibromobutane as the major product, whereas in the presence of large amounts of hydrogen bromide, 1,2-dibromobutane is obtained. A number of proposals have been made to explain this effect.

We wish to report that we are unable to substantiate the Tanner, *et al.*, claim that with low hydrogen bromide concentration 1,3-dibromobutane is the major product. Table II shows some of our findings. Therefore, we propose that, until further evidence is provided, the impact of their conclusions on the original hypothesis of bromine atom bridging in the transition state be disregarded.

It is interesting that Tanner, *et al.*,[6c] did not observe the hydrogen bromide effect in photobromination of

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[4] R. R. Pavlis, unpublished results from these laboratories.

[5] W. A. Thaler in "Methods in Free Radical Chemistry," Vol. 2, E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1970, p 151.

[6] (a) D. D. Tanner, D. D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 7398 (1969); (b) D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *ibid.*, **93**, 4802 (1971); (c) D. D. Tanner, W. M. Mosher, N. C. Das, and E. V. Blackburn, *ibid.*, **93**, 5846 (1971).

cyclohexyl bromide; even at 1.3% conversion they obtain the result earlier reported by Thaler, predominant formation of *trans*-1,2-dibromocyclohexane. The authors, however, persist in their rationalization that at still lower conversions the effect *would have been* observed.

There is no clue regarding the reasons for the effect on hydrogen bromide on product composition as claimed by Tanner, *et al.* Perhaps it is significant that raw product mixtures were injected into their gas chromatographic apparatus, without prior treatment to remove HBr and Br_2.[6a]

Acknowledgment. The financial assistance of the Air Force Office of Scientific Research is acknowledged with gratitude (Grant No. 1983).

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Photoinitiated Brominations of Butyl Bromide. On the Question of Kinetic Assistance by Neighboring Bromine[1]

Sir:

On the basis of many experiments in our laboratory during the past 3 years, we conclude, contrary to some other investigators,[2] that kinetic assistance by neighboring bromine[3] dominates the course of the liquid-phase radical reaction of bromine with butyl bromide.[4a]

The deactivating polar effect of a chloro substituent toward radical halogenation of an alkyl chain is well established.[5] When the liquid-phase bromination of alkyl bromides (including butyl bromide and cyclohexyl bromide) led to the formation predominantly (85% or more) of vicinal dibromides, these contrasting results were taken as strong evidence for kinetic assistance by the neighboring bromo substituent in the hydrogen-abstraction step.[3,6] Recently this interpretation has been challenged, and the apparent activating effect of the bromo substituent has been attributed to a difference in the rate of reaction of a bromoalkyl radical with HBr and with Br_2 at positions vicinal to and more remote from the bromo substituent in the bromoalkyl radical.[2] The product mixtures formed early during the reaction of butyl bromide with bromine were reported to consist mainly of 1,3-dibromobutane, although the final product mixture did consist mainly (85–88%) of the 1,2-dibromide.[2] As bromination proceeded, HBr accumulated in the mixture, and the reversal of the radical-forming step (*i.e.*, $R\cdot + HBr \rightarrow RH + \cdot Br$) was presumed to be faster than the reaction of $R\cdot$ with bromine and faster with the radical leading to 1,3-dibromide than with the one leading to 1,2-dibromide.[2,7]

In spite of repeated, meticulous efforts, we have been unable to reproduce these results with butyl bromide and bromine. In *every* experiment, with photoinitiation and with different personnel and reaction conditions, we have obtained product mixtures in which 1,2-dibromide is the principal product.

Our brominations have utilized a variety of reaction conditions, including slow addition of Br_2 in a nitrogen stream and batch additions of different molar equivalents of Br_2, reactions in neat butyl bromide and in CCl_4 and CH_3CN solutions, and extents of reaction ranging from less than 1% to 100%. We have deliberately chosen procedures which should favor the formation of 1,3-dibromide if HBr reversal is important,[2] and one procedure which we consider particularly definitive is described here. Small glass ampoules, which had been washed with aqueous ammonia, dried, and incorporated into a vacuum line apparatus, were covered with aluminum foil, charged with a mixture of butyl bromide and Br_2 (approximately a 3.5:1 to 7.5:1 mol ratio) prepared from reagents which were specially dried and treated to exclude HBr, degassed by a freeze–thaw method, sealed off, placed in a water bath at the selected reaction temperature, and irradiated with a 300-W incandescent lamp.[8] After different times, one by one the ampoules were removed, immediately frozen in liquid nitrogen, and opened. The contents were titrated with iodide and thiosulfate solutions for remaining bromine (extent of reaction) and analyzed by gas chromatography (gc) for mono- and dibromobutanes.[9] The data from typical experiments are summarized in Table I. Sometime after 44% reaction, HBr reversal apparently influences the product mixture composition slightly, but not so dramatically as first reported.[2]

The interpretation that selective HBr reversal is responsible for the preferential formation of 1,2-dibromides by molecular Br_2 was strongly and directly tied to the predominant formation of nonvicinal dibromides in the radical reactions of *N*-bromosuccinimide (NBS) with butyl bromide and with cyclohexyl bromide.[2,10] The hydrogen-abstracting agent was as-

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[1] A portion of the research summarized here was reported at the Reaction Mechanisms Conference, Santa Cruz, Calif., June 1970.

[2] (a) D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 7398 (1969); (b) D. D. Tanner, M. W. Mosher, N. C. Das, and E. V. Blackburn, *ibid.*, **93**, 5846 (1971); (c) D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *ibid.*, **93**, 4802 (1971).

[3] W. A. Thaler, *ibid.*, **85**, 2607 (1963); in footnote 12, this author credits Professor P. S. Skell with suggesting a neighboring group interpretation for his observations.

[4] (a) For a thorough review of radical brominations, see W. A. Thaler, *Methods Free-Rad. Chem.*, **2**, 121 (1969); (b) *ibid.*, 2, 196 (1969); (c) *ibid.*, **2**, 198 (1969).

[5] For a review, see M. L. Poutsma, *Methods Free-Rad. Chem.*, 79 (1969).

[6] P. S. Skell and P. D. Readio, *J. Amer. Chem. Soc.*, **86**, 3334 (1964), emphasize the stereochemical evidence obtained with 4-*tert*-butylcyclohexyl bromide.

[7] The separate kinetic data required to evaluate this proposal do not appear to be available, but, for other alkyl and haloalkyl radicals for which data are reported, "The rate of reaction of alkyl radical with Br_2 is considerably more rapid than the corresponding reaction with HBr."[4b] The description of the reaction makes it difficult for anyone to refute this interpretation, for failure to obtain 1,3-dibromide as the major product, even early in the reaction, can be blamed on unsuspected HBr (or any other rapidly reacting hydrogen-transfer reagent) in the initial reaction mixture.

[8] Analysis of a mixture of butyl bromide and bromine which was prepared similarly but not irradiated showed no bromination products.

[9] Samples of 1,2- and 1,3-dibromobutane mixed with bromine undergo isomerization to mixtures of the two dibromides when injected into an aluminum gc column, but no isomerization occurs with glass or Teflon-lined aluminum columns. We destroyed unreacted bromine with thiosulfate solution before chromatography of the product mixture on a 12 ft × $^1/_8$ in. Teflon-lined aluminum column packed with 10% Carbowax 20M on Chromosorb W (60–80 mesh), from which the isomers emerged in the order 1,1-, 1,2-, 1,3-, and 1,4-dibromobutanes. No 1,4-dibromide or polybromination products were detected in the bromination product mixtures.

[10] We also find that NBS bromination of butyl bromide in acetonitrile[2a] gives predominantly 1,3-dibromide during the first half of the reaction; 1,4-dibromide, absent in the Br_2 experiments described above, is a minor product in the NBS ones. Typical data which we have obtained for this reaction (essentially the same procedure as described for Br_2 reagent) are summarized in Table II.