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]

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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-

(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.

Table I. Isomeric Product Distributions Obtained from Brominations of Butyl Bromide with Molecular Bromine

Time, min	% conversion	Rel amounts of isomeric dibromobutanes[a] 1,1	1,2	1,3	Av dev, %
	25 ± 1°; BuBr:Br_2 = 6.8:1[c]				
2	1.37		7.3	1.0	1.1
4	2.95		7.3	1.0	2.1
8	6.41	0.1	7.6	1.0	1.5
16	10.5	0.1	7.5	1.0	1.4
32	22.1	0.1	7.3	1.0	1.3
64	43.5	0.1	7.3	1.0	0.98
128	75.4	0.1	8.9	1.0	1.2
	60.7 ± 1.5°; BuBr:Br_2 = 7.5:1[c]				
1	1.74	0.1	4.5	1.0	2.0
3	22.5	0.09	4.5	1.0	2.4
10	71.5	0.10	5.2	1.0	0.65
25	89.8	0.11	5.7	1.0	0.94
40	99.8	0.11	6.1	1.0[b]	1.1
	4 ± 1°; BuBr:Br_2 = 5.9:1[c]				
4	1.01	0.1	11	1.0	0.39
10	2.12	0.1	11	1.0	0.52
25	3.42	0.1	11	1.0	1.5
63	13.05	0.1	11	1.0	1.6

[a] Each line of data is the average from two to three gc injections; the average deviations are given in the last column. [b] The distribution in this line, equivalent to the ratios 1,1:1,2:1,3 = 1.4:84.7:13.9, is nearly identical, within the deviation limits specified, to that reported by Thaler.[3] [c] Mol ratio of reactants.

sumed to be the same (Br·) in both the molecular Br_2 and the NBS reactions, and the NBS was presumed to consume HBr rapidly as it was generated.[2] These two brominating reagents do show the same selectivities toward different benzylic hydrogens,[4c] but few data comparing their selectivities toward alkanic hydrogens are available. Their relative reactivities toward benzylic and alkanic hydrogens may be different;[11] that is, the hydrogen-abstracting species may be different. In fact, the relative reactivities of the various hydrogens in cyclohexyl bromide with Cl_2, with Br_2, and with NBS[2b] strongly imply that the hydrogen-abstracting radical in the NBS reaction is much closer to Cl· than to Br· in selectivity.[12] High selectivity by the attacking radical (substantial bond breaking and radical character development in the transition state) is essential for neighboring bromine participation.[4a] If the attacking radical in NBS brominations of alkanes is not Br· and is lower in selectivity than is Br·,[10,11] the difference in product distributions for NBS and Br_2 brominations of alkyl bromides[2] is comprehendible,

(11) In ref 2b, a sentence, rationalizing the different product distributions obtained from cyclohexyl bromide and NBS with photoinitiation and with AIBN initiation, reports that a bromine color developed during the more rapid photoinitiated reaction, and a portion of the bromination was attributed to utilization of the molecular bromine. Since the color developed early when plenty of NBS was available for reaction with HBr, this sentence seems tantamount to acknowledging different selectivities and different attacking radicals for the NBS and Br_2 reactions.

(12) The single publication that attacks the mechanism of *alkanic* bromination by NBS seems to be that by P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, **85**, 2850 (1963). The stereochemical data therein led to the conclusion that "the alkyl radical intermediate is not brominated by NBS, but presumably by molecular Br_2 present in steady low concentration." It seems likely at this time that NBS competes poorly with Br_2 as a chain-transfer reagent when some bromine (even at low concentration) is available for reaction. One should expect a mechanism (and selectivity) different from that with molecular Br_2 only early in the photoinitiated NBS reaction or in a radical (*e.g.*, AIBN) initiated NBS reaction, when Br_2 (and HBr) are essentially excluded. These are precisely the reaction conditions that give different product mixtures from those obtained with molecular Br_2.[2b]

Table II. Isomeric Product Distributions Obtained from Photoinitiated NBS Bromination of Butyl Bromide in Acetonitrile at 60 ± 1° (Mol ratio NBS:BuBr:CH_3CN = 1:5.9:27)

Time, min	% NBS consumed	Rel amounts of isomeric dibromides— 1,1	1,2	1,3	1,4
4	5.4	0.29	0.30	1.0	0.17
30	35.7	0.27	0.53	1.0	0.12
62	58.1	0.24	0.89	1.0	0.08
105	80.5	0.20	1.16	1.0	0.06
165	93.5	0.20	1.10	1.0	0.06
230	95.9	0.23	1.13	1.0	0.06

and the apparent relevance of the NBS reactions to the actual mechanism of molecular bromine bromination is lost. We are currently investigating the relative reactivities of a series of alkanes toward Br_2 and NBS to help clarify this point.

In summary, we believe that the interpretation[2] of the butyl bromide–bromine reaction which places paramount importance on polar deactivation and HBr reversal of the initial alkyl radical formation is erroneous and that the earlier interpretation[3] in terms of kinetic assistance by neighboring bromine is supported by the present data.

(13) (a) The original version of this manuscript was prepared while JGT was a NATO Senior Fellow in Science at the Institut für organische Chemie, Universität des Saarlandes, Saarbrücken, Germany; JGT acknowledges with appreciation the courtesies extended to him by Professor M. Hanack and the Institut. (b) JGT gratefully acknowledges the exchange of correspondence and manuscripts about this work with Professor P. S. Skell prior to publication.

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Photo-CIDNP Arising from a Minor Reaction Pathway during the Cleavage of α-Aryl Aldehydes

Sir:

The solution phase photolysis of a variety of β,γ-unsaturated aldehydes[1] leads, *via* the excited singlet state, to decarbonylation.[2] A cleavage of the α carbon–carbon bond, to form a closely associated allyl–formyl radical pair, is fully consistent with the experimental data, although a major contribution by concerted decarbonylation has not been excluded. The available data on the photolysis of α-aryl aldehydes suggest that decarbonylation proceeds from an excited singlet state in this system as well.[3] Thus, excitation (3130 Å) of the n → π* transition of 2-methyl-2-phenylpropanal (I) leads to cumene (Φ = 0.76) in a reaction shown by deuterium labeling to be predominantly intramolecular. The amount of bicumyl formed (18% of the cumene formed at 0.01 *M* I) decreases with decreasing concentration of I. This reaction is not quenched by *cis*-

(1) Photo-CIDNP has been observed for aromatic aldehydes by Cocivera and Trozzolo and by Closs and Paulson. Polarization in these cases, however, results from the intermolecular reaction of triplet excited state aldehydes leading, in the case of benzaldehyde, to a benzoyl–hydroxybenzyl radical pair: (a) M. Cocivera and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 1772 (1970); (b) G. L. Closs and D. R. Paulson, *ibid.*, **92**, 7227 (1970).

(2) E. Baggiolini, H. P. Hamlow, and K. Schaffner, *ibid.*, **92**, 4906 (1970).

(3) H. Küntzel, H. Wolf, and K. Schaffner, *Helv. Chim. Acta*, **54**, 868 (1971).