Radical Brominations of Alkanic Positions by Bromine and by *N*-Bromosuccinimide[1]

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Abstract: On the basis of the following data, we conclude that the mechanisms of radical brominations of alkanic systems by Br_2 and by NBS are different. Photoinitiated competitive brominations of butyl bromide–cyclohexane and of cyclopentane-cyclohexane mixtures with Br_2 and with NBS give product ratios differing by factors of 11 and 5, respectively, with no change in the isomer distributions obtained with single substrates. Photoinitiated reaction of Br_2 with cyclopropane gives 1,3-dibromopropane, while that of NBS with cyclopropane gives cyclopropyl bromide, showing that different attacking radicals are generated from the two Br reagents. Photoinitiated reactions of norbornane with Br_2 and with NBS give different ratios of exo-2:endo-2 bromides, showing that the bromine-transfer reagent which reacts with 2-norbornyl radical is different for the two Br reagents.

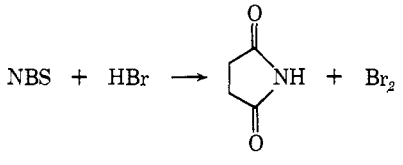
During the past decade the details of the mechanism of radical bromination of alkanes, and in particular the influence of a bromo substituent on the selectivity in the hydrogen-abstraction step, have been studied and debated by several groups of investigators.[2-5] Radical reactions of alkyl bromides with molecular bromine generally produce mixtures of dibromides in which the vicinal dibromide predominates. This selectivity was first attributed to kinetic assistance by the bromo substituent[2] but later was claimed to result from the relative rates of reaction between the isomeric bromoalkyl radicals and hydrogen bromide.[3] The data on which this latter interpretation was based have been disputed by us[5] and others[4] and finally retracted.[3d] In the same article as the retraction, the interpretation persists, however, and rests on new data reported for reactions in large excesses of bromine.[3d]

Central to the controversy is the mechanism of bromination by *N*-bromosuccinimide (NBS), for some of the proposals[3] are supported almost solely by the presumed sameness of bromination mechanism for both molecular bromine and NBS reagents. That sameness

$$Br_2 \rightleftharpoons 2Br\cdot$$

$$R{-}H + Br\cdot \rightleftharpoons R\cdot + HBr$$

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot$$



was established for brominations of benzylic positions by kinetic studies[6] and has been assumed for other systems.[3] Some earlier data in the literature on bromocyclohexane halogenations[3b] indicate that the isomer distribution obtained with NBS reagent is closer to that obtained with Cl_2 than to that with Br_2, even though the data were presented from the viewpoint that Br_2 and NBS brominations involve the same hydrogen-abstracting and bromine-transfer species. In order to reconcile differences in product distributions that we obtained from brominations of butyl bromide by these two reagents, however, we recently suggested that different mechanisms are involved with alkanic positions.[5] That is, the hydrogen-abstracting agent is different when molecular bromine is used than when NBS is used. This report summarizes our further investigation of this point. Both by intermolecular competition experiments (butyl bromide *vs.* cyclohexane and cyclohexane *vs.* cyclopentane) and by reactions with single substrates (cyclopropane and norbornane), the two brominating reagents have been shown to be different. With cyclopropane, the identity of the generated radical which attacks substrate is shown to be different, and with norbornane, the identity of the bromine-transfer reagent which reacts with the alkyl radical is shown to be different.

Butyl Bromide *vs.* Cyclohexane. An equimolar mixture of butyl bromide and cyclohexane was brominated with a 0.1 mol equiv of molecular bromine or of NBS. With bromine, the product ratio was approximately 11 times the ratio obtained with NBS. Butyl bromide reacts faster than cyclohexane with bromine (BuBr: C_6H_{12} = 2.3:1) but slower than cyclohexane with NBS (BuBr:C_6H_{12} = 0.20:1). With both reagents, the dibromobutane isomer distribution was the same as that obtained under the same conditions with butyl bromine substrate alone.[5]

The intermediate radicals, $\dot{C}_4H_8Br$ and $\dot{C}_6H_{11}$, are formed by competitive hydrogen abstractions and react competitively with the source of substituent bromine. If reversal of the hydrogen abstraction is unimportant, the product ratio, $C_4H_8Br_2/C_6H_{11}Br$, is concordant with the relative rates of hydrogen abstraction from the two substrates. The reversal reaction may occur to substantially different extents with the two intermediate radicals, however, because of the possibility of unfavorable interactions between the bromobutyl radical (more polar than the unsubstituted cyclohexyl radical)

(1) Presented in part at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, Abstract ORGN 25, and in part at the 28th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., Dec 1972, Abstracts, Paper 214.

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

(3) (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); (d) D. D. Tanner, J. E. Rowe, T. Pace, and Y. Kosugi, *ibid.*, **95**, 4705 (1973).

(4) P. S. Skell and K. J. Shea, *J. Amer. Chem. Soc.*, **94**, 6550 (1972).

(5) J. G. Traynham, E. E. Green, Y.-S. Lee, F. Schweinsberg, and C.-E. Low, *J. Amer. Chem. Soc.*, **94**, 6552 (1972).

(6) (a) R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 354 (1963); (b) G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963); (c) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963).

and polar HBr.[3d] This kind of difference in reaction of radical intermediates with HBr would lead to a bromination product which indicates a higher relative rate of substitution into butyl bromide than that which would be indicated in the absence of HBr reversal. Thus, the difference in relative rates of bromination of the two substrates by molecular bromine and by NBS is consistent with different mechanisms but, in the absence of other data, is not compelling evidence for them.

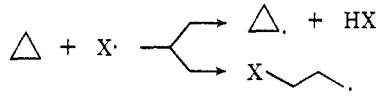
We find that irradiation of an equimolar butyl bromide–cyclohexane mixture in a large excess (100 mol equiv) of bromine does produce a product mixture indicative of a substantially increased relative reactivity of cyclohexane[3d] ($C_4H_9Br:C_6H_{12}$ = 1:3.1 at 60°). Some *trans*-1,2-dibromocyclohexane is also formed (no isomers detected), and the dibromobutane isomer distribution is the same as that obtained with 0.1 mol equiv of bromine. An alkyl bromide alone probably provides, by internal competition, a better test of the importance of hydrogen bromide reversal than does the competition between different substrates in bromine solvent. With butyl bromide, the ratio, 1,2-$C_4H_8Br_2$:1,3-$C_4H_8Br_2$, did not decrease when we changed from 0.1 mol equiv of bromine to 100 mol equiv of bromine and interrupted the reaction after about 3% of the butyl bromide reactant had been converted. Polybromination does not occur under these conditions. Were hydrogen bromide reversal important and faster with less polar radicals (bromo substituent more remote from radical center) than with more polar ones,[3] and were excess bromine able to override that reaction as claimed,[3d] higher proportions of 1,3-dibromobutane would be expected with large excesses of bromine than with 0.1 mol equiv. Since we do not obtain that result, hydrogen bromide reversal must play little or no role in the proportions of dibromobutanes formed.[7]

We cannot now account to our own satisfaction for the fact that the change from a brominating mixture which is largely hydrocarbon to one which is largely bromine changes cyclohexane from a less reactive to a more reactive competitor with butyl bromide. The over-all results, however (*viz.*, cyclohexyl bromide faster than cyclohexane and the essentially unchanged dibromide isomer distribution), do not fit or support the interpretation[3d] that selective hydrogen bromide reversal (reduced or eliminated in excess bromine) is enhancing the apparent reactivity of the alkyl bromide with respect to the cyclohexane.

Cyclohexane *vs.* Cyclopentane. Cyclohexane and cyclopentane undergo chlorinations at different relative rates ($k_{C_5H_{10}}/k_{C_6H_{12}}$ = 0.85 at 68°).[8] In radical brominations, these two substrates yield intermediate cycloalkyl radicals, both of which are unsubstituted and are expected to show little if any difference in reactivity toward HBr. Competitive brominations of this pair of hydrocarbons at 60° with molecular bromine give relative reactivity ratios of $C_5H_{10}:C_6H_{12}$ = 7.0 (RH:R′H:Br_2 = 10:10:1) and 8.0 (RH:R′H:Br_2 = 1:1:100) and some *trans*-1,2-dibromocyclopentane; with NBS the relative reactivity ratio is 1.6, and no bromide is formed. The change from hydrocarbon to bromine solvent does affect the $C_5H_{10}:C_6H_{12}$ reactivity ratio slightly, but the change is an increase; the ratio is clearly not reduced[3d] to that obtained with NBS.

The similarity of the chlorination rates was attributed to the small extent of bond breaking at the transition state (small extent of eclipsing strain relief).[8] The substantially different rates for bromination by molecular bromine are consistent with the greater extent of bond breaking expected at the transition state for hydrogen abstraction by Br· than by Cl·. It is difficult to rationalize these data with any mechanism which specifies that the hydrogen-abstracting species is the same for Br_2 and NBS reagents.

Cyclopropane. Cyclopropane undergoes liquid phase radical halogenations to give substitution product (cyclopropyl halide) and ring-opening product (1,3-dihalopropane). The proportions of these competitively formed products depend on the identity of the halogenation reagent. With chlorine as reagent (Cl· chain), the ratio of cyclopropyl chloride:1,3-dichloropropane is about 1:4 at 0° and about 1.5:1 at 68°.[9] With *tert*-butyl hypochlorite (*t*-BuO· chain), however, the ratio is at least 17:1 at both 0 and 68°.[9] In an early study which established the radical character of the reaction between cyclopropane and bromine (Br· chain), 1,3-dibromopropane, the only product identified, was obtained in high yield.[10] Under the same conditions, hydrogen bromide (Br· chain) also gave only ring-opening product (propyl bromide).[10] It is clear and unsurprising that different radical reagents (Cl·, *t*-BuO·, and Br·) give quite differing proportions of hydrogen abstraction and ring-opening processes with cyclopropane.[11]



When we carried out photoinitiated brominations of cyclopropane ($C_3H_6:Br_2$ = 10:1 mol ratio) in methylene chloride solution at 0°, only 1,3-dibromopropane was obtained; no cyclopropyl bromide was detected by gas chromatography. (There was no reaction under these conditions in the dark.) Even with an irradiated solution of cyclopropane in liquid bromine (approximately 0.1 mol equiv of C_3H_6), 1,3-dibromopropane was the sole product detected. When we used NBS (C_3H_6:NBS = 10:1 mol ratio) in acetonitrile solution, however, >98% of the product mixture was cyclopropyl bromide. These completely opposite ratios of products from Br_2 and NBS reactions must mean that *different chain-carrying radicals* (Br· and presumably succinimidyl) are generated from the two reagents. One (Br·) reacts exclusively by attack on carbon (to give ring opening), but the other, like *tert*-butoxy radical, abstracts hydrogen predominantly. The relative energies of the alternative pairs of bonds formed and

(7) By private communication, Professor P. S. Skell and J. C. Day (Pennsylvania State University) have informed us that they have confirmed these observations with butyl bromide and have extended the investigation to 1-bromoheptane, which likewise gives essentially unvarying proportions of (five) isomeric dibromoheptanes over widely differing substrate:Br_2 ratios (10:1 to 1:100), with and without NBS present.

(8) R. Srinivasan and F. I. Sontagg, *Can. J. Chem.*, 47, 1627 (1969).

(9) C. Walling and P. S. Fredricks, *J. Amer. Chem. Soc.*, 84, 3326 (1962).

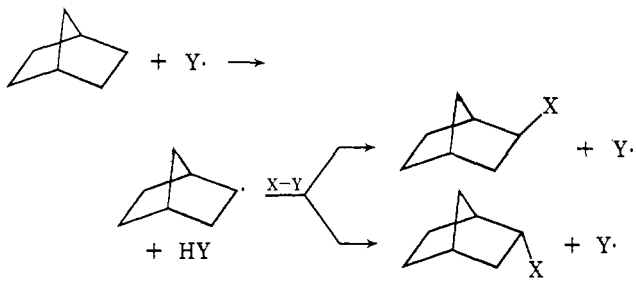
(10) M. S. Kharasch, M. Z. Fineman, and F. R. Mayo, *J. Amer. Chem. Soc.*, **61**, 2139 (1939).

(11) The regioselectivity[12a] and stereochemistry[12] of the ring-opening bromination of substituted cyclopropanes have been studied recently.

(12) (a) K. J. Shea and P. S. Skell, *J. Amer. Chem. Soc.*, **95**, 6728 (1973); (b) G. G. Maynes and D. E. Applequist, *ibid.*, **95**, 856 (1973).

broken (X–C/C–C *vs.* X–H/H–C) undoubtedly determine the alternative pathways for reaction, but the data required for a "prediction" when X = succinimidyl are not available to us.

Norbornane. Norbornane undergoes chlorination with a variety of chlorinating reagents to give mainly a mixture of *exo*- and *endo*-2-chloronorbornane whose composition is dependent on the identity of the chlorine-transfer agent which reacts with the 2-norbornyl radical intermediate.[13] Although the exo/endo ratio is related to the size of the chlorine-transfer reagent, the order of probable steric requirements of these reagents does not coincide with the order of exo/endo ratios.



The important aspect for our present consideration, however, is that the exo/endo ratio is different for different halogen-transfer reagents and *is unaffected by any reversal of the radical-forming step.* No matter how substantial or little is the reversal reaction with HBr, it is difficult to see how that reaction can have any effect on the exo/endo product ratio obtained from brominations. If the bromine-transfer species are the same, the same stereoisomeric product ratio will be obtained. Conversely, if different exo/endo product ratios are obtained with different brominating reagents, the bromine-transfer species must be different.

When norbornane was photobrominated with molecular bromine (0.14 mol equiv in Freon 113 solution), no 1-bromonorbornane was detected in the product mixture, and the exo/endo ratio of 2-bromonorbornanes was 2.1.[14] When NBS was used as the brominating reagent (0.15 mol equiv in CH_2Cl_2 solution), some 1-bromonorbornane (8.0%) was found in the product mixture, and the exo/endo ratio of 2-bromonorbornanes was 3.6. When 2-bromonorbornane was prepared by the Kochi reaction[15] (2-norbornanecarboxylic acid, lead tetraacetate, sodium bromide), the exo/endo ratio of 2-bromonorbornanes formed from the 2-norbornyl radical intermediate was 1.8.

With Br_2, a small amount of a mixture of isomeric dibromides was formed, along with the monobromides, but the product distribution pattern (gc) was quite different from that obtained by reaction of Br_2 with norbornene.[16,17] It seems rather certain then that these dibromides are formed by radical substitution into the monobromides rather than by an HBr elimination–Br_2 addition sequence. When a mixture of 2-bromonorbornanes (exo/endo = 1.8) was brominated with Br_2 (0.067 mol equiv), the bromine was consumed faster than it was with norbornane under the same conditions, and the same mixture of dibromides was formed. The exo/endo ratio of reactants remained constant, however, within the precision of the gc measurements, throughout the course of the bromination. Thus, the exo/endo product ratio obtained from norbornane and Br_2 is reliable and unaffected by the small amount of dibromination which occurred.

These results establish that bromination of norbornane by Br_2 and by NBS involve *different bromine-transfer species*, different mechanisms. We believe that the original reagent is the bromine-transfer agent with both molecular bromine and NBS and that all available information favors this conclusion for other alkanic systems.

Discussion

These data demonstrate that radical brominations of *alkanic* positions by Br_2 and by NBS proceed by *different* mechanisms.[18] Yet the evidence that the *same* mechanism (Br· chain) occurs with *benzylic* positions is equally compelling.[6] How can we reconcile these results?

The transition state for hydrogen abstraction by bromine atom involves considerably more bond breaking (and a higher activation energy) than the one for hydrogen abstraction by chlorine atom.[19] The reactivity ratio for toluene/cyclohexane at 80° is 60 for bromination but 0.091 for chlorination.[19] For bromination, but not for chlorination, the C–H bond breaking with toluene is sufficient to allow substantial stabilization of the transition state by benzylic resonance, compared with the alkanic system, cyclohexane. The electronic effect of *gem*-phenyl actually slows hydrogen abstruction by chlorine atom.

NBS dissociation can potentially initiate either a bromine atom or succinimidyl radical chain. With alkanic systems (at least the ones we have examined,[20] without exception), the succinimidyl chain appears to have the lower activation energy and is the one which occurs. The selectivity patterns indicate that, as with Cl·, little C–H bond breaking has occurred at the transi-

(13) (a) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, 4, 382 (1958); (b) P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, 3, 177 (1970).

(14) Previous workers[13a] reported that bromination of norbornane with bromine in boiling carbon tetrachloride (80°) gave an exo/endo product ratio of 3 (only the exo product was actually determined), that use of $BrCCl_3$ (AIBN initiation) gave an exo/endo product ratio of 5.3, and that use of NBS (AIBN initiation) gave a low conversion to impure product for which an exo/endo ratio could not be determined.

(15) (a) J. K. Kochi, *J. Amer. Chem. Soc.*, 87, 2500 (1965); *J. Org. Chem.*, 30, 3265 (1965); (b) for a review of decarboxylations by lead tetraacetate, see R. A. Sheldon and J. K. Kochi, *Org. React.*, 19, 279 (1972).

(16) D. R. Marshall, P. Reynolds-Warnhoff, E. W. Warnhoff, and J. R. Robinson, *Can. J. Chem.*, 49, 885 (1971).

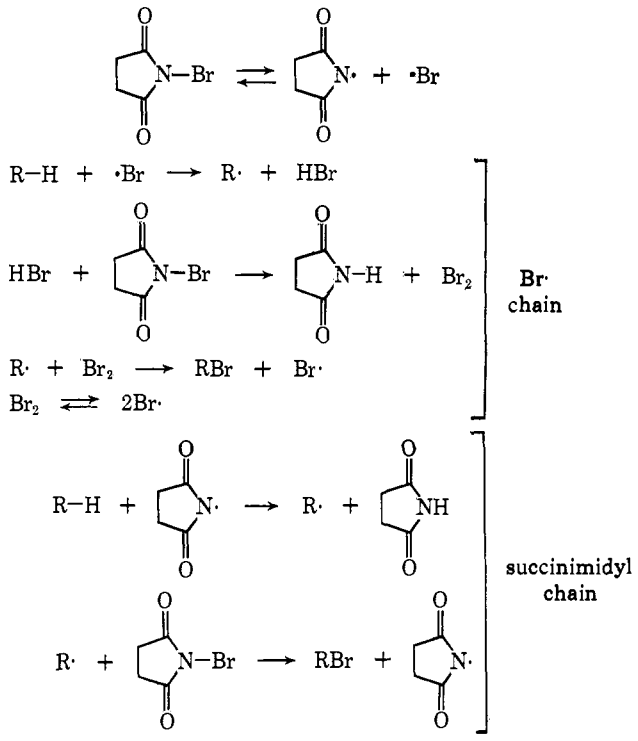
(17) We did not attempt to determine the absolute or even relative yields of all the isomeric dibromonorbornanes because such data would have required a substantial amount of experimental work that would have made no contribution to the issue of Br_2 *vs.* NBS mechanisms.

(18) To support the same mechanism for Br_2 and NBS, the relative reactivity data for some pairs of alkanic substrates reacting with different *N*-bromoamides have been discussed as though they were independent of the identity of the amide.[3d] The rate ratios that are most precisely reported, however (chlorocyclohexane:cyclohexane), actually show a threefold range for the four *N*-bromo amides used, quite outside the reported uncertainty in the data. The data actually suggest rather strongly that different hydrogen abstracting radicals are involved. A similar variation actually appears also in the data reported (C. Walling and A. L. Rieger, *J. Amer. Chem. Soc.*, 85, 3134 (1963)) for the relative reactivities of ethylbenzene:toluene and methylcyclohexane:toluene with the different *N*-bromo amides.

(19) (a) For a thorough review of radical brominations, see W. A. Thaler, *Methods Free-Radical Chem.*, 2, 121 (1969); (b) G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, 77, 4578 (1955).

(20) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, 85, 2850 (1963). Data in this paper indicate that the bromine atom chain may be favored for attack on a tertiary alkyl position with vicinal bromine. This preference may result from the increased radical character on the tertiary carbon at the transition state, allowing stabilizing interaction with the neighboring bromine.

tion state for succinimidyl attack, and little resonance stabilization of the transition state from benzylic systems is to be expected. As is true for chlorine atom, then, succinimidyl radical will, we believe, react less readily with benzyl systems than with alkanic ones. With benzylic systems, the alternate, bromine atom chain becomes favored, because of stabilization in the transition state.



Photodissociation of NBS under our conditions (tungsten lamp) is far slower and less efficient than is photodissociation of bromine, and transfer of bromine from NBS to alkyl radical is slow.[20] Therefore, in mixtures containing both bromine and NBS, bromine atom generation will far exceed succinimidyl radical generation. These mixtures give alkanic product distributions substantially the same as those obtained with bromine alone rather than those obtained with NBS alone.[4,7] In a mixture of bromine and NBS, the bromine atom chain does not diminish the concentration of bromine nor the efficiency of generation of bromine atoms.

Experimental Section

Gas chromatographic (gc) analyses were obtained with a Hewlett-Packard Model 700 instrument equipped with a flame-ionization detector and 0.125-in. Teflon-lined columns packed with 10% Carbowax 20M or 10% QF-1 on 60–80 mesh Chromosorb P (acid washed). Preparative gc separations were accomplished with a Varian Aerograph Model 90-P instrument equipped with a 5 ft × 0.25 in. column packed with 10% Carbowax 20M on 60–80 mesh Chromosorb W (acid washed). Proton nuclear magnetic resonance (nmr) spectra were obtained with a Varian Associates Model A60A and a Perkin-Elmer R12 spectrometer; samples were examined as 10–20% solutions in carbon tetrachloride with tetramethylsilane as internal reference.

Reagents. Commercial, reagent grade bromine was distilled (in flame-dried apparatus) through a short column (bp 59°). The middle portion of distillate was collected, stored over phosphoric anhydride, and redistilled in a similar manner immediately before use. *N*-Bromosuccinimide was recrystallized from hot water and stored over calcium chloride in a desiccator with protection from light. Titration with standard aqueous thiosulfate showed the NBS to be 99.8% pure. Commercially available substrates and solvents were purified before use in the bromination experiments by recommended procedures.[21]

General Procedure for Brominations. The brominations were carried out in small Pyrex ampoules (i.d. 8.5 mm except for experiments with excess bromine, for which i.d. 17 mm ampoules were used) which had first been cleaned with acid–dichromate solution; washed with water, with concentrated aqueous ammonia, and again with water; dried in an oven; and covered with aluminum foil. Ampoules were charged with a mixture of compound(s) to be brominated, brominating reagent (Br_2 or NBS), and solvent (if one were used); incorporated into a vacuum line apparatus and degassed by a freeze–thaw method; sealed off; placed in a water bath at the selected reaction temperature; and irradiated with a 300 W clear incandescent lamp 30 cm from the ampoules. After different times, the ampoules were removed, immediately frozen in liquid nitrogen, and opened. Except for the experiments in which a large excess of bromine was used, a portion of the reaction mixture (1.0 ml) was added to a mixture of 10% aqueous potassium iodide (10 ml), Freon 113 (1 ml), and 1 *M* hydrochloric acid (2 ml). The liberated iodine was titrated with standard thiosulfate solution to determine the extent of reaction, and the Freon 113 solution was analyzed by gc methods for product distribution.

For the experiments with a large excess of bromine, the reaction mixture was diluted with Freon 113 (1 ml) and then added to ice-cold aqueous thiosulfate solution. The mixture was centrifuged to remove precipitated sulfur, and the Freon 113 solution was analyzed by gc methods.

The identities of products in the mixtures were established by comparison of gc retention times with purchased or separately prepared authentic samples. Product distributions reported are averages of at least two separate experiments.

Butyl Bromide–Cyclohexane Competitions. A. Deficiency of Br_2. Mixtures (~2 ml) of $C_4H_9Br:C_6H_{12}:Br_2$ = 10:10:1 (mol ratio) were irradiated at 60 ± 1° and became colorless (*i.e.*, 100% reaction) after 11 min. Gc analysis revealed a product distribution (mol ratio, ±0.2 max), 1,1-$C_4H_8Br_2$:1,2-$C_4H_8Br_2$:1,3-$C_4H_8Br_2$:$C_6H_{11}Br$:*trans*-1,2-$C_6H_{10}Br_2$ = 1.1:49.9:11.1:37.9:trace. These data give the reactivity ratio $C_4H_9Br:C_6H_{12}$ = 2.30:1. The mole ratio among the $C_4H_8Br_2$ isomers alone was 1,1:1,2:1,3 = 0.1:6.2:1.0 (lit.[5] 0.11:6.1:1.0).

B. **Excess Bromine.** Mixtures of $C_4H_9Br:C_6H_{12}:Br_2$ = 1:1:100 were irradiated at 60 ± 1° for 10 and 20 min (1 and 3% consumption of C_4H_9Br, respectively). Gc analysis showed an average product distribution (mol ratio, ±<0.1) of 1,1-$C_4H_8Br_2$:1,2-$C_4H_8Br_2$:1,3-$C_4H_8Br_2$:$C_6H_{11}Br$:*trans*-1,2-$C_6H_{10}Br_2$ = trace:20.5:4.0:60.7:14.8 (1,2-$C_4H_8Br_2$:1,3-$C_4H_8Br_2$ = 5.1:1). These data give the reactivity ratio $C_4H_9Br:C_6H_{12}$ = 0.33:1. Parallel experiments without C_6H_{12} present ($C_4H_9Br:Br_2$ = 1:100) produced the $C_4H_8Br_2$ average product distribution 1,1:1,2:1,3 = 1.6:82.6:15.8 (0.1:5.2:1).

C. **NBS.** Mixtures of $C_4H_9Br:C_6H_{12}:CH_3CN$ = 10:10:26.5 were saturated with NBS at 25° (<1 mol equiv) and irradiated at 60 ± 1°. After 75 min, 98% of the NBS had reacted. Gc analysis revealed the average product distribution (mol %, ±0.3 max) 1,1-$C_4H_8Br_2$:1,2-$C_4H_8Br_2$:1,3-$C_4H_8Br_2$:1,4-$C_4H_8Br_2$:$C_6H_{11}Br$ = 1.5:8.3:6.6:0.5:83.1. These data give the reactivity ratio $C_4H_9Br:C_6H_{12}$ = 0.20:1. The relative amount among the $C_4H_8Br_2$ isomers alone was 1,1:1,2:1,3:1,4 = 0.2:1.3:1.0:0.07 (lit.[5] 0.23:1.13:1.0:0.06.)

Cyclopentane–Cyclohexane Competitions. A. Deficiency of Br_2. Ampoules containing about 2 ml of a mixture of $C_5H_{10}:C_6H_{12}:Br_2$ = 10:10:1 (mol ratio) were irradiated at 60 ± 1° until the mixture became colorless (*i.e.*, 100% reaction). Gc analyses showed the average product distribution (mol %, ±0.5 max) C_5H_9Br:*trans*-1,2-$C_5H_8Br_2$:$C_6H_{11}Br$:*trans*-1,2-$C_6H_{10}Br_2$ = 72.4:14.8:12.8:trace. The dibromides were counted with the corresponding monobromides for calculating the reactivity ratio $C_5H_{10}:C_6H_{12}$ = 6.8:1.

B. Excess Bromine. Ampoules containing mixtures of $C_5H_{10}:C_6H_{12}:Br_2$ = 1:1:100 were irradiated for 70 sec at 60 ± 1°. Gc analysis revealed that 2.1% of the C_6H_{12} had been consumed and that the average product distribution (mol %, ±0.3 max) was C_5H_9Br:*trans*-1,2-$C_5H_8Br_2$:$C_6H_{11}Br$:*trans*-1,2-$C_6H_{10}Br_2$ = 71.8:17.1:10.0:1.1. The dibromides were counted with the corresponding monobromides for calculating the reactivity ratio $C_5H_{10}:C_6H_{12}$ = 8.0:1.

(21) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley, New York, N. Y., 1970.

C. NBS. Mixtures of C_5H_{10}:C_6H_{12}:NBS:CH_2Cl_2 = 10:10:1:132 were irradiated at 60 ± 1° for 1 hr (reaction 99% complete). The product distribution (mol %, ±0.2) was C_5H_9Br:$C_6H_{11}Br$ = 62.3:37.7, from which the reactivity ratio was calculated to be C_6H_{10}:C_6H_{12} = 1.65:1.

Cyclopropane. A. Deficiency of Bromine. Ampoules chilled in liquid nitrogen were charged with cyclopropane (18 mmol) and then with a solution of bromine in CH_2Cl_2 (mol ratio C_3H_6:Br_2:CH_2Cl_2 = 10:1:8.6). The solutions were irradiated at 0 ± 1° until colorless (6 hr). Gc analysis revealed 1,3-dibromopropane as the only product. When a similar mixture of cyclopropane and bromine was treated in the same way except not irradiated, no bromination products could be detected by gc analysis.

B. Excess Bromine. Chilled ampoules were charged with cyclopropane (0.65 mmol) and bromine (65 mmol) and irradiated at 0 ± 1° for 30 min or for 90 min. For both reaction times, gc analysis revealed only 1,3-dibromopropane product; no bromocyclopropane was detected.

C. NBS. Chilled ampoules were charged with cyclopropane (40 mmol) and then with an acetonitrile solution of NBS (mol ratio C_3H_6:NBS:CH_3CN = 10:1:9.4). At 0°, some NBS precipitated, but it disappeared during irradiation at 0 ± 1°. Irradiation was continued for 10 hr; titration showed that all the NBS had reacted. Gc analysis revealed <2% 1,3-dibromopropane and >98% bromocyclopropane as the only products.

Brominations of Norbornane and Bromonorbornanes. A. Norbornane + Br_2.[14] Mixtures of norbornane:Br_2:Freon 113 = 7:1:16 (mol ratio) were irradiated at 60 ± 1° until colorless (4.5 hr). Gc analysis revealed an average product distribution (±1% max), *exo*-2-bromonorbornane:*endo*-2-bromonorbornane = 68:32 (exo/endo = 2.1), plus a small amount of a mixture of dibromonorbornanes.[22]

B. 2-Bromonorbornane Mixture + Br_2. A mixture of 2-bromonorbornanes (exo/endo = 1.8) was brominated in Freon 113 solutions at 60 ± 1° (mol ratio, substrate:Br_2:Freon 113 = 15:1:75). Ampoules were opened and analyzed after 54% (6 min), 79% (13 min), 98% (25 min), and 100% (40 min) reaction. The gc patterns for the dibromonorbornane mixture were the same as that obtained in the experiments with norbornane, and the exo/endo ratio of 2-bromonorbornanes remained 1.8 at all stages of the bromination. A similar reactant mixture left at 60 ± 1° for 4 hr without irradiation did not give gc detectable amounts of bromination products, and the exo/endo ratio remained 1.8.

C. Norbornane + NBS. Mixtures of norbornane:NBS:CH_2Cl_2 = 6.8:1:117 (mol ratio) were irradiated at 60 ± 1° for 4.5 hr. Titration showed that no NBS remained, and gc analysis revealed a mixture of bromonorbornane isomers with an average product distribution (±0.8 max) of *exo*-2-:*endo*-2-:1- = 72:20:8.0 (exo/endo = 3.6).

Authentic Product Samples. Reagent grade commercial samples of **1,2-, 1,3-, and 1,4-dibromobutane, bromocyclohexane, *trans*-1,2-dibromocyclohexane, bromocyclopentane, bromocyclopropane, and 1,3-dibromopropane** were used as gc standards without further purification. **1,1-Dibromobutane**[23] was prepared from silver 2-bromopentanoate and bromine:[23] bp 65–66° (20 mm); nmr (CCl_4) δ 5.70 (t, 1, J = 6.2 Hz, $CHBr_2$), 2.37 (m, 2, CH_2CBr_2), 1.60 (m, 2, CH_3CH_2), 0.98 (m, 3, CH_3). ***trans*-1,2-Dibromocyclopentane**[24] was prepared by addition of bromine to cyclopentene in carbon tetrachloride: bp 85–87° (23 mm). ***exo*-2-Bromonorbornane**[25] was prepared in 64% yield by the addition of HBr (from 48% hydrobromic acid) to norbornene: bp 86–87° (31 mm);[25a] nmr δ 3.9 (*endo*-HCBr).[25b] ***endo*-2-Bromonorbornane** was prepared from norbornene by hydroboration,[26] treatment of the borane with bromine and sodium methoxide in methanol,[26] and selective solvolysis of *exo*-bromide with 80% aqueous ethanol at 55°:[27] bp 69–71° (15.5 mm).[27] Gc analysis revealed some contaminants (no *exo*-2-bromide) that were not removed by further distillation, so a sample of pure *endo*-2-bromide was collected by preparative gc: nmr δ 4.2 (*exo*-HCBr).[25b] A mixture of *exo*- and ***endo*-2-bromonorbornanes** (exo/endo = 1.8) was prepared by the lead tetraacetate oxidation[15] of *exo*-2-norbornanecarboxylic acid in refluxing benzene solution containing sodium bromide (20 mmol each of acid, lead tetraacetate, and sodium bromide in 20 ml of benzene). **1-Bromonorbornane** was prepared from norbornanone[28] (mp 89–91°) through 2,2-dibromonorbornane. The dibromide (bp 78.5–80° (1.5 mm); nmr (CCl_4) all absorptions at δ 3.5–0.9), which was prepared in 51% yield from the ketone and phosphorus pentabromide,[29] was reductively rearranged to 1-bromonorbornane by stirring with anhydrous aluminum bromide in a mixture of pentane and isopentane;[30] the product mixture contained, in addition to the 1-bromide, *exo*-2- and *endo*-2-bromides (gc identification) and dibromonorbornanes (bp and nmr spectral indication). The desired 1-bromide was purified by preparative gc: nmr, all H absorptions between δ 2.4 and 1.0.

(22) Most of the components in this mixture of dibromonorbornanes had the same relative retention times, but not the same proportions, as a mixture prepared by addition of bromine to norbornene in CCl_4 solution.[16,17] The gc analysis of the addition mixture we prepared corresponded to that reported.[16]

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