On the Mechanism of *N*-Bromosuccinimide Brominations. Bromination of Cyclohexane and Cyclopentane with *N*-Bromosuccinimide

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The competitive *N*-bromosuccinimide (NBS) bromination of cyclopentane vs. cyclohexane was shown to proceed by a mechanism dominated by either a bromine atom chain, a succinimidyl chain, or a mixed chain. The dominance of each of the major chain-carrying processes depends upon the solvents used, to some degree upon the reactivity of the substrate, and upon the additives (molecular bromine or ethylene) used to moderate or enhance one or the other of the chain processes. No evidence was obtained, from studies of the NBS halogenation of the two substrates used, which required the intermediacy of an excited-state succinimidyl radical to explain the reactivities obtained. The observation that β-bromopropionyl isocyanate is produced under all of the reaction conditions precludes the requirement that brominations using the NBS–Br_2 reagent proceed exclusively by a radical species whose reactions do not correlate with a ring-opening process.

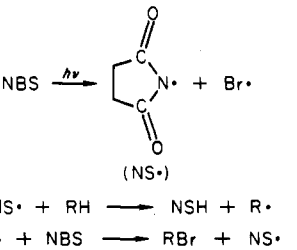
The mechanism of the *N*-bromosuccinimide (NBS) halogen substitution reaction has been the subject of a number of investigations; however, a definitive reaction scheme has yet to be established.[2] The question as to whether the mechanism involves the succinimidyl radical, (Scheme I, the Bloomfield mechanism)[3] or the bromine atom, (Scheme II, the Goldfinger mechanism)[4] as the chain-carrying species is still a matter of some controversy. The mechanism has been further complicated by the proposal that more than one abstracting succinimidyl radical (σ or π) is necessary to explain the reactivity of the reagent toward a variety of substrates.[5] The postulate of a radical species capable of undergoing a chain reaction, in solution, from two electronic states was a unique suggestion.[5] It has been proposed that NBS forms a σ-succinimidyl radical when it transfers with an energetic primary or secondary alkyl radical (eq 1) and a π radical when

$$\text{NBS} + \text{R}\cdot\ (\text{primary or secondary}) \rightarrow \text{RBr} + \sigma\text{-NS}\cdot \quad (1)$$

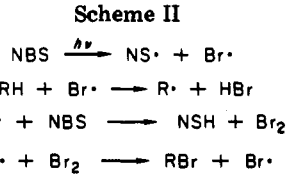
$$\text{NBS} + \text{Br}\cdot \rightarrow \text{Br}_2 + \pi\text{-NS}\cdot \quad (2)$$

it transfers with a bromine atom[5a,b] (eq 2) or with a stabilized alkyl radical.[5c,d] Although the primary pathway for the reaction (50–70%) of the σ-NS· radical[5] is the β-scission reaction (Scheme III), it was suggested that the fraction of the reaction (4%) that undergoes substitution does so with a radical selectivity that is different than that observed with molecular bromine or when the NBS reactions are run under reaction conditions that presumably lead to the formation of π-NS·.[5] The π-NS· radical, presumably, does not lead to the β-scission product since the ring-opening process does not correlate with ground-state succinimidyl.[5]

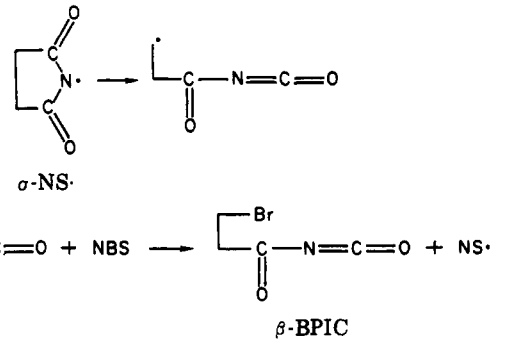
Scheme I



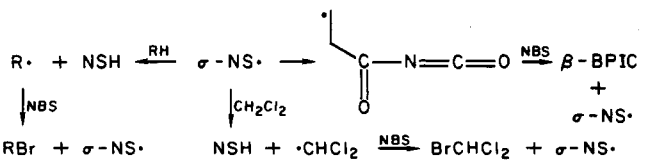
Scheme II



Scheme III



Scheme IV



It has been proposed that, in the case of the reactions carried out under conditions where transfer of NBS does not take place with a bromine atom (added olefin), the energetics of the carbon-centered radical which transfers with NBS determines whether the succinimidyl radical is formed in the π or σ state.[5c] When these reactions are carried out in solvent methylene chloride the σ radical

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(2) (a) Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 3142. (b) Walling, C.; Rieger, A. L.; Tanner, D. D. *Ibid.* **1963**, *85*, 3129. (c) Russel, G. A.; Desmond, K. M. *Ibid.* **1963**, *85*, 3139. (d) Tanner, D. D.; Rowe, J. E.; Pače, T.; Kosugi, Y. *Ibid.* **1973**, *95*, 4705. (e) Traynham, J. G.; Lee, Y. S. *Ibid.* **1974**, *96*, 3590. (f) Day, J. C.; Lindstrom, M. J.; Skell, P. S. *Ibid.* **1974**, *96*, 5616.

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formed from the reaction of an energetic radical will react with methylene chloride, ring open, or react with substrate (see Scheme IV). The ratios of $BrCHCl_2/\beta$-BPIC in these systems are reported to be independent of the concentration or reactivity of the substrate (RH) as long as R· is a primary or secondary radical.[5c,d]

Traynham and Lee[2e] had previously proposed that the chain-carrying species operative in the NBS bromination reactions depended upon the substrate that was being halogenated. The report proposes that a bromine atom chain governs the reaction during benzylic halogenation (previously reported[2a-c]) while a succinimidyl chain controls the reactivity of alkanes. This conclusion was reached, for the mechanism operating for the halogenation of alkanes, primarily from a comparison of the relative rates of bromination of 1-bromobutane vs. cyclohexane and cyclohexane vs. cyclopentane with both molecular bromine and NBS. These conclusions were also based in part on the differences between the ratio of products obtained from the bromination of cyclopropane (solvent acetonitrile) and norborane (solvent acetonitrile) with NBS or with molecular bromine.

It had been reported[2d] that the relative rates of bromination of 1-bromobutane vs. cyclohexane with molecular bromine were a function of the concentration of the bromine used. At high concentrations of molecular bromine the relative rates of bromination were the same as with NBS in acetonitrile, 0.5, while at lower concentrations of bromine (0.5 mol of bromine to 1.0 mol of substrate) the 1-bromobutane reacted 3.7 times faster than the cyclohexane. Similar results were obtained, although unexplained, by Traynham and Lee[2e] in their later study. They chose for their comparison with NBS the relative rates of bromination with molecular bromine at low concentrations and reached the conclusion that the two chain-carrying species were different.

An explanation for the variation in relative reactivity with the concentration of molecular bromine, suggested in the original paper,[2d] was confirmed by independent studies on the separate substrates 1-bromobutane[6] and cyclohexane,[7] subsequent to the publication by Traynham. The studies on cyclohexane showed that under typical conditions for bromination (5:1 RH/Br_2, complete reaction), the reversal reaction of the cyclohexyl radical with hydrogen bromide and hydrogen tribromide completely dominated the bromination sequence prior to the formation of products. The studies on 1-bromobutane revealed that the reversal reactions of the deactivated radicals formed in the bromination of 1-bromobutane are not very important processes. The differences in the observed competitive rates of bromination of these two substrates with molecular bromine under different concentration conditions can be rationalized as being due to reactions involving hydrogen bromide. The results of the direct comparison of the relative rates of bromination of cyclohexane vs. 1-bromobutane with high concentrations of molecular bromine and with NBS in acetonitrile would be consistent with a bromine atom chain without reversal, while under the conditions used by Traynham for comparison the relative reactivities would appear to be different even if both reactions were due solely to bromine atom abstraction.

The distributions of dibrominated products obtained in the NBS bromination of both 1-bromobutane and cyclohexyl bromide, in acetonitrile, have been reported to be a function of the concentration and percentage conversion of the halogenating agent.[8] It had also been demonstrated[2d] that the competitive brominations of several substrate alkanes showed the same relative reactivity with mixtures of NBS–Br_2 as with brominations carried out with large excesses of NBS. Although the former observation was confirmed by Traynham,[9] and it was likewise concluded that mixtures of NBS–Br_2 would most likely result in a bromine atom chain,[2e] these observations were not included in the evaluation of the proposed mechanism for the NBS bromination of alkanes. Originally,[8] it was thought that hydrogen bromide reversal was the cause of the change in the product distribution observed for the NBS halogenation of 1-bromobutane. Since this reaction was later shown not to be an important process for this substrate even with molecular bromine,[6] it is clear that in order to explain the change in reactivity during the NBS bromination of 1-bromobutane in acetonitrile a mechanism which involves more than one abstracting species must be invoked. A tentative mechanism which is consistent with these observations can be suggested. At high concentrations of NBS in acetonitrile, when the reaction is carried out to low conversion, a succinimidyl radical would be the dominant chain-carrying species, but as the reaction proceeds and the concentration of free bromine increases the product distribution changes to resemble that found for molecular bromine. The change in mechanism may be enhanced by the transfer process given in eq 3.

$$NS\cdot + Br_2 \rightarrow NBS + Br\cdot \qquad (3)$$

The present study was undertaken to establish whether the reactivity of NBS is a function of the substrate used, as had been proposed,[2e] or whether it is a function of the conditions (solvent and concentration) under which the reaction is carried out. The suggestion[5] that the succinimide radical undergoes reactions from two different electronic states was also investigated.

Results

In the course of the mechanistic studies of NBS halogenations, a number of solvents have been employed: Freon 113, carbon tetrachloride, benzene, methylene chloride, and acetonitrile. The latter three solvents had been chosen in preference to the first two because the reagent was soluble in both acetonitrile and methylene chloride and slightly soluble in benzene. Table I lists a comparison of the relative rates of bromination of two typical alkanes with NBS (cyclopentane relative to cyclohexane) in these solvents.

Originally, small amounts of molecular bromine were added to the NBS halogenation mixtures in order to ensure the dominance of the bromine atom as the chain propagating species.[2d] In the solvents Freon and benzene the relative rates of bromination, k_5/k_6, are unaffected by the addition of small amounts of bromine while in methylene chloride or acetonitrile the addition of bromine changes the relative reactivities to higher values, and eventually the relative rates of bromination correspond to those obtained with molecular bromine[10] (see Table II).

In order to limit the incursion of the bromine atom chain, one can include the addition of small amounts of olefin which lack an allylic hydrogen in the reaction mix-

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(8) Tanner, D. D.; Mosher, M. W.; Das, N. C.; Blackburn, E. V. *J. Am. Chem. Soc.* **1971**, *93*, 5846.
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(10) Tanner, D. D.; Ruo, T. C.-S.; Takiguchi, H.; Guillaume, A. *Can. J. Chem.* **1981**, *59*, 1368.

Table I. Effect of Solvent on the Relative Rates of Bromination of Cyclohexane (k_6) and Cyclopentane (k_5) with NBS (23 °C)

solvent[c]	10 [reactants], mol/L			% reaction[b]	k_5/k_6[a]
	$[C_5H_{10}]$	$[C_6H_{12}]$	[NBS]		
Freon 113	7.15	9.80	0.498	76	9.94
	7.98	8.10	0.508	49	9.44
benzene[d]	5.15	5.49	0.331	100	9.16
	8.02	8.02	0.512	66	8.24
methylene chloride	5.09	4.77	0.395	100	1.78 ± 0.04 (3)
	4.91	5.04	0.405	39	1.04
acetonitrile	7.03	7.59	0.511	100	1.12
	8.00	7.96	0.494	64	0.95
	7.10	7.58	0.437	50	0.79
	7.03	7.59	0.511	43	0.76

[a] The numbers in parentheses are the numbers of independent experiments. The errors are the average errors from the mean value listed. [b] Percentage reaction was determined by titration for active halogen prior to GLC analysis. [c] In two of the solvents, acetonitrile and Freon, a faint color of bromine developed during the course of the reaction. After titration with thiosulfate the color was discharged. [d] The absolute yield of brominated cycloalkanes was very low (~2.2% for cyclopentyl bromide and ~0.3% for cyclohexyl bromide). No dibrominated product was detected, since kmost of the NBS reacts by addition to solvent (see ref 5c).

ture. This technique, to limit the amounts of halogenation atoms available to initiate a halogen atom chain, has been used in other studies of halogenation reactions which were thought to proceed by mixed chain mechanisms such as the reactions of reagents like *tert*-butyl hypochlorite[11] and NBS.[2b,f]

Competitive NBS brominations of cyclohexane and cyclopentane were carried out in the presence of added ethylene (see Table III).

Discussion

The effect of solvent on the relative rates of bromination of the cycloalkanes can be seen in Table I. The relative reactivities, k_5/k_6, are divided into two categories, depending upon the solvent used; one in which cyclopentane is brominated 9–10 times faster than cyclohexane and one in which the two hydrocarbons are brominated at nearly the same rate. The higher of the two relative reactivity ratios is nearly identical with the ratio reported for the bromination rates of the two hydrocarbons with molecular bromine, in the absence of hydrogen bromide (see Table II).

The lower relative reactivity ($k_5/k_6 \approx 0.8$) obtained for the halogenations in acetonitrile is therefore attributed by elimination to a less selective succinimidyl radical chain. The explanation for the change in reactivity with solvent can be found in a communication concerning the mechanism of allylic bromination.[2f] Because of high solubility of the reagent in the solvents methylene chloride and acetonitrile, the concentration of NBS remains high and the succinimidyl chain remains dominant while in solvents where the NBS is insoluble only the bromine atom chain can proceed since radical transfer with the solid NBS is slow. A limitation was placed on the suggested mechanism for these halogenations.[2f] The succinimide chain was claimed to proceed only in the presence of olefinic materials, and the bromine atom chain quickly takes over the propagation sequence for the substitution of alkanes in the absence of olefins.[2f] This limitation appears to be contradictory to conclusions reached by Traynham and Lee[2e] and is not entirely consistent with the data presented in Table I for the bromination carried out in methylene chloride or acetonitrile, although the relative reactivities obtained in these solvents do change somewhat during the course of the reaction. The rate of change from a succinimidyl to a bromine atom chain is undoubtedly dependent upon the facility with which the particular substrates react with the two chain-carrying radicals.

The change in relative reactivity of cyclopentane vs. cyclohexane during the course of their NBS brominations in methylene chloride or acetonitrile is shown in Table I. As the concentration of NBS remaining in solution diminished the relative reactivity increased. Although this change in selectivity was not as dramatic as had previously been observed for other substrates,[8] the previous suggestion that hydrogen bromide affected even the kinetics of NBS brominations could be tested. The possible inclusion of a reversible step was eliminated since the competitive bromination of cyclohexane and perdeuteriocyclohexane with NBS in acetonitrile or methylene chloride with and without added bromine did not show detectable incorporation of protium into the unbrominated deuteriocyclohexane or deuterium incorporation into the unbrominated cyclohexane (eq 4–6; see Experimental Section).

$$C_6D_{11}\cdot + (D)HBr \rightleftarrows C_6D_{11}H + Br\cdot \quad (4)$$

$$C_6H_{11}\cdot + (H)DBr \rightleftarrows C_6H_{11}D + Br\cdot \quad (5)$$

$$R\cdot + R'D(H) \rightleftarrows RD(H) + R'\cdot \quad (6)$$

Since reversible abstraction during the reactions of NBS can be ruled out as a factor that contributes to the dependence of the relative rate ratio upon the percentage reaction, the most reasonable explanation is that the bromination can proceed by a mixed chain. As the concentration of NBS decreases its rate of transfer with an alkyl radical becomes slower, and the concentration of succinimidyl radicals that are generated decreases. Abstraction by a bromine atom, generated from the small amounts of bromine formed during the reaction, begins to be competitive with succinimidyl radical abstraction, and the reaction becomes increasingly dominated by the bromine atom chain. The change in mechanism may be facilitated by a transfer reaction between the NS· radical and molecular bromine (eq 3).

The relative rates, determined from the results of an analysis of the products of the brominations carried out in the various solvents, were all lower when the reactions were carried out in the presence of olefin than when the rate ratios were determined without its addition.

The lower values represent the selectivity of the succinimidyl radical and presumably in all solvents this selectivity is that of the ground-state radical. In the reactions carried out in a solvent which favors the bromine atom chain (Freon), the addition of ethylene appears to change the mechanism to a chain dominated by succinimidyl

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Table II. Effect of Added Bromine on the Relative Rates of Bromination of Cyclopentane (k_5) and Cyclohexane (k_6) with NBS (23 °C) in a Variety of Solvents

solvent	10[reactants], mol/L				products, mol/mol of NBS reacted × 100			mass balance, %		
	$[C_5H_{10}]$	$[C_6H_{12}]$	[NBS]	$[Br_2]$	NSH	β-BPIC	RBr	NS	Br	k_5/k_6
Br_2[a]	0.608	0.604		140–180						9.20 ± 0.28
vapor[a]	1.2×10^{-4}	6.5×10^{-4}		47×10^{-4}						9.66 ± 0.26
Freon 113	7.15	9.80	0.498							9.94
	5.96	8.16	0.417	4×10^{-2}						10.1
benzene	5.15	5.46	0.331							9.16
	4.28	3.94	0.446	11×10^{-2}						11.2 ± 0.5 (2)
methylene chloride	8.10	8.21	1.03		56.5 ± 1.4	38.9 ± 3.2	53.8 ± 0.3	95.4 ± 4.6	92.7 ± 3.5	1.77 ± 0.01 (3)
	4.27	4.34	0.394	1.85×10^{-2}	69.6 ± 1.4	30.1 ± 3.0	67.3 ± 1.4	99.7 ± 4.4	97.4 ± 4.4	4.40 ± 0.33 (3)
	4.27	4.34	0.359	9.78×10^{-2}	87.8 ± 3.2	10.0 ± 4.0	90.7 ± 2.5	97.8 ± 7.2	101 ± 6.5	8.52 ± 0.23 (4)
acetonitrile	7.96	7.62	1.00		77.2 ± 1.0	17.5 ± 1.6	73.9 ± 1.6	94.7 ± 2.6	91.4 ± 5.2	1.12 ± 0.04 (3)
	4.18	4.13	0.402	4.27×10^{-2}	84.4 ± 3.6	17.5 ± 3.2	85.3 ± 1.9	102 ± 6.8	103 ± 5.1	4.85 ± 0.23 (3)
	4.40	3.88	0.381	9.09×10^{-2}	92.2 ± 0.2	8.0 ± 1.0	92.3 ± 0.7	100 ± 1.2	100 ± 0.3	8.74 ± 0.05 (2)

[a] Taken from ref 10. [b] The errors reported are average deviations from the mean value obtained. The numbers in parentheses are the number of independent experiments carried out. [c] RBr calcd as [RBr + $2RBr_2$ + $CHCl_2Br$ (if done in CH_2Cl_2 solvent)]. [d] The reactions carried out with added bromine were run until from 40–96% of the active halogen was used. Under these conditions the products reported did not vary more than the experimental limits listed. The remaining active halogen was always greater than the initial concentrate of added bromine.

Table III. Effect of Added Olefin on the Relative Rates of Bromination of Cyclopentane (k_5) and Cyclohexane (k_6) with NBS (23 °C)

solvent	10[reactants], mol/L				% reacn[a]	product yield, %				material balance,[d] %		β-BPIC/$CHCl_2Br$ ratio	k_5/k_6
	$[C_5H_{10}]$	$[C_6H_{12}]$	[NBS]	$[C_2H_4]$		RBr[b]	$C_2H_4Br_2$[c]	β-BPIC[d]	NSH	NS	Br		
Freon 113	7.15	9.80	0.498		76	100					100		9.94
	24.4	24.7	2.70	1.73	61	25.5	1.28	30.9	67.8	98.7	98.1		0.91
	24.4	24.7	2.81	1.59	63	24.0	1.20	36.1	62.1	98.2	99.5		0.88
methylene chloride	8.10	8.21	1.03		100	53.8 ± 0.3		38.9 ± 3.2	56.5 ± 1.4	95.4 ± 4.6	92.7 ± 3.8	24/1	1.77 ± 0.01 (3)
	24.7	24.1	2.99[e]	1.83	100	60.2	2.64	33.3	69.0	102.3	98.7	22/1	0.83
	8.09	7.46	0.998	0.658	100	53.7	3.26	(40.4)[f]	62.7	103.1	97.4	25/1	0.80
	8.02	8.00	0.964	0.292	100	56.9 ± 0.6	3.45	(36.1 ± 0.2)[f]	63.8 ± 2.4	98.8 ± 3.3	96.6 ± 1.0	19/1	0.82 ± 0.1 (2)
acetonitrile	7.96	7.62	1.00		100	73.9 ± 1.6		17.5 ± 1.6	77.2 ± 1.0	94.7 ± 2.6	91.4 ± 5.2		1.12 ± 0.04 (3)
	8.36	7.82	1.02	0.580	100	71.0	1.59	25.7	72.3	98.0	99.9		0.78
	8.36	7.82	1.02	0.722	100	80.5	1.57	16.4	83.7	99.9	100		0.78

[a] Calcd as ([NBS]° − [NBS]^f/[NBS]°) × 100. [b] Calcd as ([RBr]/[NBS]° − [NBS]^f) × 100; reactions in methylene chloride without ethylene include 1.6 ± 0.03% bromodichloromethane as one of the brominated materials used to calculate [RBr]. [c] Calcd as 2([$C_2H_4Br_2$]/[NBS]° − [NBS]^f) × 100. [d] ([Moles of product]/[NBS]°) × 100. [e] The [NBS]° used somewhat exceeded its solubility at this temperature (0.20). [f] Values reported were obtained from the integrated 200-MHz ^{1}H NMR spectrum.

radical propagation. In the reactions carried out in solvents which favor the succinimide chain (methylene chloride and acetonitrile), the small amount of an admixed bromine atom chain reaction which takes place is effectively inhibited by the addition of ethylene, and the relative reactivity of the succinimidyl radical is observed ($k_5/k_6 \simeq 0.8$).

With the NBS–Br_2 reagent, the cycloalkanes undergo halogenation by utilizing the bromine atom chain, while with the NBS–olefin reagent, the succinimidyl radical is the dominant chain-carrying species.

The duality of reactions proposed for the succinimidyl radical (σ and π radicals) is based not only on the belief that the two electronic states show a different relative reactivity during competitive halogenations but also on the fact that only the σ radical generated in the presence of ethylene can yield the β-scission product, β-bromopropionyl isocyanate (β-BPIC).[5] It can be seen from the results listed in Table III that the NBS brominations carried out with and without added olefin yielded the same (within experimental error) ratios of β-BPIC/$BrCHCl_2$, ~25/1. Since under the conditions (NBS–Br_2) proposed to be necessary to generate the π radical substantial (~20%) yields of β-BPIC are formed, one must conclude that, if two states of the radical exist, with this system they are chemically indistinguishable (see Table III) or that the system is not as clearly understood as the initial publications infer.[5]

Experimental Section

Materials. Perdeuteriocyclohexane (Merck Sharp & Dohme, Canada) was used without further purification. GLC analysis showed it to be >99.9% pure, and mass spectral analysis (AEI MS-50, 12 eV) showed it to contain 99.47 atom % D.

Cyclopentane (Phillips 66, research grade) and cyclohexane (Aldrich Chemical) were heated to reflux over P_2O_5 and fractionally distilled by using an 18-in. Vigreux column, and the middle fractions were collected. GLC analysis showed them to be >99.9% pure.

Freon 112 (PCR) and Freon 113 (Matheson of Canada Ltd.) were fractionally distilled (18-in. Vigreux column) from P_2O_5; the middle fractions were collected.

Bromine (Fisher Scientific) was washed twice with concentrated sulfuric acid, decanted, and fractionally distilled (18-in. Vigreux column) from P_2O_5. The middle fraction was collected.

N-Bromosuccinimide (Fisher Scientific Co.) was recrystallized from hot water. Titration showed it to be more than 99.5% pure.

Ethylene (Matheson, research grade >99.98%) was distilled before use.

Acetonitrile (MCB) was purified by successive distillations over potassium permanganate and sodium carbonate. The distillate was treated with several drops of concentrated sulfuric acid and redistilled. Finally, it was distilled again over calcium hydride.

Benzene (American Chemicals Ltd.) was dried over sodium wire and distilled prior to use. GLC analysis showed it to be >99.9%.

Methylene chloride (Caledon Chemical Co.) was dried over calcium chloride and distilled using a 3-ft Teflon spinning-band column. GLC analysis showed it to be 99.98% pure. Traces of chloroform were detected.

Bromination of Cyclopentane and Cyclohexane with NBS. Aliquot samples of solutions or mixtures of weighed quantities of NBS and the two substrates or of the two substrates and an internal standard (hexachloroethane) dissolved in the suitable solvent were placed in Pyrex ampules. The reaction vessels were degassed by the freeze–thaw method, in the absence of light, and thermostated at 23 ± 0.5 °C. After equilibration, the tubes were irradiated with incandescent light through the (9 mm) Pyrex thermostat for an appropriate period of time (approximately 16 h for 50% reactions). The reaction vessels were then quenched in liquid nitrogen and subjected to iodometric titration. An aliquot of a standard solution containing two external standards, *o*-dichlorobenzene and chlorobenzene, was added, and the organic mixture was analyzed by GLC with either a 50-m methylsilicone capillary column, a 10 ft × $^1/_8$ in. stainless steel column packed with 5% Ucon Polar HB50 2000 on Chromosorb PAW, or a 24 ft × $^1/_4$ in. 7% SE-30 on Chromosorb PAW stainless steel column. The area ratios obtained from the chromatograms were determined by using a Hewlett-Packard intergrator. The molar ratios of products to standards were determined from standard calibration curves. When the reactions were carried out in acetonitrile, the standard was added as a solution in *n*-pentane so that the organic and aqueous phases were immiscible. Control experiments on synthetic product mixtures added to the reaction mixtures but isolated and analyzed without irradiation showed that the analytical procedure was accurate. Preanalyzed synthetic reaction mixtures, without brominating reagent, were irradiated, subjected to the analytical procedure, and found to give the same ratios of products (within the experimental errors quoted) as were found in the preanalyzed samples.

The reactions carried out with added bromine (irradiation times of 0.1–2 h for complete reaction) were carried out in an identical manner except that aliquots of standard solutions of molecular bromine in the required solvent were added to the reaction mixtures. The reactions with added bromine were carried out to various degrees of completion. The reactions were stopped when the active halogen remaining was still >$[Br_2]$°.

The dibrominated cycloalkane, 1,2-dibromopentane, amounted to 7.1 ± 0.9% of the bromocyclopentane (CH_2Cl_2 solvent) and 3.3 ● 0.7% of the cyclopentyl bromide when the reactions were carried out in acetonitrile. Only traces of dibrominated cyclohexane were detected. When the reactions were carried out in CH_2Cl_2 as the solvent, 2.3 ± 0.5% of the active bromine produced $CHCl_2Br$.

The reactions run with added ethylene (irradiation times of ~20 h for 50% reaction) had manometrically measured amounts of ethylene transferred to the reaction vessel while the ampule was still attached to the vacuum line.

Bromination of Cyclohexane and Perdeuteriocyclohexane with NBS and NBS–Br_2. The reactions were carried out and analyzed in the same mammer as were the reactions of cyclohexane vs. cyclopentane. The molar concentration of $NBS/C_6H_{12}/C_6D_{12}$ (0.079:0.071:0.071) or $NBS/Br_2/C_6H_{12}/C_6D_{12}$ (0.079:0.014:0.071:0.071) (~50% reaction) ensured the best chance of observing any exchange reactions.

The unhalogenated hydrocarbons were isolated by preparative GLC (SE-30 column), and the mixture of cyclohexane and perdeuteriocyclohexane was subjected to mass spectral analysis (AEI MS-2). A sample of the initial mixture of cyclohexane and perdeuteriocyclohexane and a sample of the mixture isolated after the reaction had identical mass spectral distributions of deuterated and protiated materials.

Analyses of β-Bromopropionamide and Succinimide. For reactions where NBS had reacted to 100% completion, a standard, butyramide, valeramide, or hexanamide, was added to the product mixture, and the solution was analyzed by using a 50-m methylsilcone capillary column (150–170 °C).

For reactions where NBS had reacted to <100% completion, the percentage reaction was determined by iodometric titration with aqueous thiosulfate. The aqueous solution was separated from the organic layer. The water was distilled under reduced pressure, a standard was added to the residue, and the material which was soluble in acetonitrile was analyzed on the 50-m methylsilicone capillary column (150–170 °C). Control experiments on standard mixtures of products substantiated the validity of the analytical procedure.

As indicated in Table III the [β-BPA] was also determined from the integrated areas of the methylene protons of β-BPA vs. NSH. The [NSH] had previously been determined by GLC. Fourier transform H^1 NMR (40 scans, CD_2Cl_2 as solvent) gave product yields of β-BPA which were within experimental error of those determined by GLC.

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Registry No. *N*-Bromosuccinimide, 128-08-5; cyclopentane, 287-92-3; cyclohexane, 110-82-7; bromine, 7726-95-6; ethylene, 74-85-1; atomic bromine, 10097-32-2; succinimidyl radical, 24344-83-0; β-bromopropionyl isocyanate, 18926-24-4.