64.5–65.5 °C; ^{1}H NMR (60 MHz, Me_2SO-d_6) δ hydroxy ether 3.68 (m, H_β, H_{OH}), 4.12 (m, H_α), 8.47 (s, Ar H); complex 4.16 (s, H_α, H_β), 7.80 (s, Ar H); UV (H_2O) λ_{max} 599 nm (ε 1.5 × 10^4).

1-(2-Hydroxyethoxy)-2,6-dinitro-4-(trifluoromethyl)benzene (3-CF_3). 2,6-Dinitro-4-(trifluoromethyl)chlorobenzene (Pierce) (4.0 g, 0.015 mol) was dissolved in 10 mL of anhydrous ether, whereupon 42 mL of a 0.4 M (10% mol excess) of a $NaOCH_2CH_2OH/HOCH_2CH_2OH$ solution was added. The resulting mixture was stirred vigorously overnight at room temperature. The crude product was isolated as described for **3**-Cl. Repeated recrystallization from water yielded pale yellow needles: mp 99.5–100 °C; ^{1}H NMR (60 MHz, Me_2SO-d_6 + concentrated HCl) δ 4.30 (m, H_α), 3.60 (m, H_β), 8.72 (s, Ar H) (note: hydroxyl proton obscured by H_2O); ($CDCl_3$) δ 4.40 (m, H_α), 3.78 (m, H_β), 3.36 (s, H_{OH}), 8.75 (s, Ar H); UV (H_2O) λ_{max} 528 nm (ε 2.3 × 10^4).

1-(2-Hydroxyethoxy)-2,6-dinitro-4-((trifluoromethyl)sulfonyl)benzene (3-SO_2CF_3). In a flask containing 250 mg (0.758 mmol) of **1**-SO_2CF_3 dissolved in a minimum volume of Me_2SO was added a 5% excess of freshly prepared 2.45 M sodium glycolate solution (0.32 mL). The solution was allowed to stand overnight, whereupon it was acidified, water was added, and it was cooled to effect precipitation. The yellowish brown amorphous solid was collected and dissolved in hexane. The hot mother liquor was separated from an insoluble oil that forms and the product crystallized from hexane as white needles (49 mg): mp 88–89 °C; ^{1}H NMR (60 MHz, $CDCl_3$) hydroxy ether δ 4.34 (m, H_α), 3.86 (m, H_β), 3.35 (s, H_{OH}), 8.67 (ArH); (Me_2SO-d_6) complex 4.20 (s, H_α, H_β), 8.94 (s, ArH); UV (H_2O) λ_{max} 470 (ε 1.1 × 10^4).

Kinetics. The slow reactions were measured with a Gilford 2000 spectrophotometer, the fast ones with a Durrum–Gibson stopped-flow apparatus. Evaluation of the first-order plots was by standard procedures; reproducibility was usually in the range 1–3%. pH measurements, accurate within ±0.01 unit, were carried out with a Corning 110 pH meter; the pH in the stopped flow experiments was measured in mock mixing experiments.

Acknowledgment. This work was supported by Grants CHE77-27998 and CHE80-24261 from the National Science Foundation.

Registry No. **1**-SO_2CF_3, 19822-29-8; **1**-NO_2, 606-35-9; **1**-CN, 19018-96-3; **1**-SO_2CH_3, 39880-50-7; **1**-CF_3, 317-70-4; **2**-SO_2CF_3, 35298-04-5; **2**-NO_2, 12128-30-2; **2**-CN, 25549-13-7; **2**-SO_2CH_3, 40203-26-7; **2**-CF_3, 28933-97-3; **3**-SO_2CF_3, 83547-68-6; **3**-NO_2, 6478-31-5; **3**-CF_3, 83547-69-7; **3**-Cl, 83547-70-0; **5**-SO_2CF_3, 83547-66-4; **5**-NO_2, 54846-61-6; **5**-CF_3, 83547-67-5; **5**-Cl, 83560-63-8; A, 123-09-1; B, 706-29-6; C, 407-16-9; D, 383-11-9; E, 1550-27-2; F, 360-00-9; 1,4-dichloro-2,6-dinitrobenzene, 2213-82-3; 2,6-dinitro-4-(trifluoromethyl)-chlorobenzene, 393-75-9.

Supplementary Material Available: Tables S1-S5, observed pseudo-first-order rate constants (6 pages). Ordering information is given on any current masthead page.

Excited-State σ Succinimidyl and Glutarimidyl Radicals: Reversible Ring Opening

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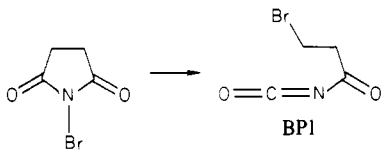
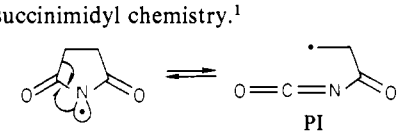
Abstract: The free-radical isomerization of *N*-bromosuccinimide to β-bromopropionyl isocyanate has been examined. Of the two varieties of succinimidyl radical (S_π or S_σ), only the σ excited state undergoes the ring opening to the β-propionyl isocyanatyl radical. The conversion optimally takes place in >95% yield. The dependence on NBS concentration along with results obtained from deuterium labeling studies indicate that the ring opening of S_σ is a reversible process. This explains the failure of *N*-chlorosuccinimide to produce β-chloropropionyl isocyanate, as well as the increase in ring-opened product for *N*-bromosuccinimides upon methyl substitution at the 2- and/or 3-position of the succinimidyl ring, since the open-chain radical intermediates are more stable. In the *N*-bromoglutarimide system, methyl groups on the 2-position are required for the glutarimidyl radicals to undergo the isomerization, ultimately producing isocyanates. The radical-chain nature of these systems is confirmed.

The rearrangement of *N*-bromosuccinimide to β-bromopropionyl isocyanate (BPI) was recognized early as a radical



NBS

process, but only recently have the numerous puzzling aspects of this reaction fallen into a framework consistent with the known S_π and S_σ succinimidyl chemistry.[1]



S_σ

$$PI + NBS \rightarrow BPI + S_\sigma$$

The isomerization of NBS to BPI was reported (1957) independently by Johnson and Bublitz[3] and Martin and Bartlett.[4] The reaction was inititated by benzoyl peroxide, and this led to the conclusion that the isomerization could be described as a radical-chain process with PI as the radical intermediate. The radical-chain character is now confirmed (vide infra) for the ring opening and the other addition and substitution reactions attributed to succinimidyls.[1]

In an important theory paper that received little attention, Koenig and Wielesek (1975)[5] suggested that ground-state succinimidyl and some of its excited states could be described as S_π and S_{σ_N} or S_{σ_O}, respectively, and that only the excited-state S_{σ_N} and S_{σ_O} had symmetries that correlated with the open-chain radical, PI. The energy sorting of these states by the INDO calculation was recognized to be of little value other than to point to the possibility that the energy separation was small.

(1) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381–387.
(2) Slanga, J. P.; Day, J. C.; Skell, P. S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 7.
(3) Johnson, H. W.; Bublitz, D. E. *J. Am. Chem. Soc.* **1958**, *80*, 3150.
(4) Martin, J. C.; Bartlett, P. D. *J. Am. Chem. Soc.* **1957**, *79*, 2533.
(5) Koenig, T.; Wielesek, A. *Tetrahedron Lett.* **1975**, 2007.

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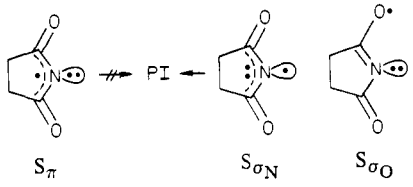


Unaware of this calculation, we had reached the conclusion, based on kinetic evidence, that two different succinimidyl radicals were required to explain the chemistry observed in thermal chain reactions, one of the sucinimidyls from the reaction of NBS with an alkyl radical, the other from the reaction of NBS with a bromine atom.[6] The conditions for these thermal chain reactions included (a) bromine scavenging to obtain the alkyl radical carrier or (b) bromine presence to obtain the bromine atom carrier. These two succinimidyl radicals showed strikingly different selectivities in competitive H abstractions from neopentane and methylene chloride (substrates that are essentially unreactive toward Br·). Further, the succinimidyl radical produced from NBS + Br· showed no tendency to undergo ring opening, while the one from NBS + R· underwent extensive ring opening. With the Koenig and Wielesek symmetry argument concerned with ring opening, the succinimidyl from NBS + Br· was assigned the S_π configuration and the succinimidyl from NBS + R· the S_{σ_N} (or S_{σ_O}).

The best thermochemical estimate[7] indicated reaction 1 was thermoneutral. If reaction 2 had produced S_π, the exothermicity

$$\text{NBS} + \text{Br}\cdot \rightarrow \text{Br}_2 + \text{S}_\pi \not\rightarrow \text{PI} \qquad (1)$$

$$\text{NBS} + \text{R}\cdot \rightarrow \text{RBr} + \text{S}_\sigma \rightarrow \text{PI} \qquad (2)$$

would have been the difference in bond strengths for 1°R–Br and Br–Br, 20–25 kcal/mol. This value sets an upper limit to the S_σ–S_π energy separation if endothermic chain steps are to be avoided.[1,6]

Selectivities for H abstractions, alkene additions, and reactions with arenes are similar for ·OH, ·Cl, and S_σ.[1,8,9] Since ·OH bimolecular rate constants are near the encounter-controlled limit,[8] in the absence of better evidence, rates of 10^7–10^9 L mol^{-1} s^{-1} are attributed to the S_σ reactions. Since the rate of the ring-opening reaction of S_σ was closely competitive with these bimolecular reactions, ring opening was assigned a rate of 10^7–10^9 s^{-1}.[2]

The suppression of the rearrangements of NBS to BPI by Br_2 was recognized,[1,23] as well as the increase in rearrangement yield which resulted from inclusions of small amounts of alkenes.[3,23,26] However, the rationalization of these observations was not the central concern of those publications.

Scope of the Isomerization. The characterization of β-bromopropionyl isocyanate by the earlier workers[3,4] in this field included the conversions to β-bromopropionamide and methyl *N*-(β-bromopropionyl)carbamate. BPI is readily recognized by its intense absorption in the infrared[3,4] at 2245 cm^{-1}. BPI is more volatile than NBS and succinimide; thus it can be separated readily from reaction mixtures by vacuum trap-to-trap distillation at room temperature. The ^{1}H NMR spectrum of BPI makes an AA′XX′ pattern (δ 3.05, 3.55) clearly distinguishable from the NBS singlet (δ 2.80) and the succinimide singlet (δ 2.65). This makes possible absolute product analysis of reaction mixtures by employing a suitable internal standard.

The best reaction conditions for the conversion of NBS to BPI include methylene chloride solvent, sufficient suitable alkene to scavenge bromine (ethylene, 3,3-dimethyl-1-butene, or 1,1-dichloroethylene), and initiation thermally with benzoyl peroxide or UV irradiation through either quartz or Pyrex. Conversions in excess of 95% can be attained by irradiation of a suspension of NBS in methylene chloride (NBS solubility = 0.22 M) containing 1,1-dichloroethylene (0.06 M). The suspended material goes into solution as the reaction progresses; the only other products are $BrCHCl_2$ (bromination of CH_2Cl_2 solvent) and succinimide (SH) in equal amounts. These results are in accord with Scheme I.

Table I

form isocyanate	no ring opening
NBS	NCS
NIS	2,3-Me_2-NCS
2,2-Me_2-NCS	NCG[a]
2,2-Me_2-NBS	NBG[a]
2,3-Me_2-NBS	3,3-Me_2-NCG[a]
2-Me-NBG[a]	3,3-Me_2-NBG[a]
2,2-Me_2NBG[a]	NCP[b]
	NBP[b]
	NIP[b]
	N-bromohydantoins

[a] G = glutarimide. [b] P = phthalimide.

Table II. Effect of Changing NBS Concentration[a] (CH_2Cl_2/CCl_4 Solvent, Neopentane Substrate (0.73 M))[b]

CH_2Cl_2/ CH_2Cl_2 + CCl_4[c]	[NBS][d]	*neo*-$C_5H_{11}Br$ mmol	*neo*-$C_5H_{11}Br$ %	BPI mmol	BPI %	BPI/ *neo*-$C_5H_{11}Br$[e]
1.00	0.145	0.085	7.4	1.07	92.6	12.6
0.86	0.100	0.120	7.7	1.44	92.3	12.0
0.70	0.049	0.180	9.4	1.73	90.6	9.6
0.51	0.023	0.110	13.6	0.70	86.4	6.4
0.28	0.010	0.075	21.1	0.28	78.9	3.7

[a] 2.25 mmol of NBS; all reaction mixtures remained heterogeneous, ensuring constant NBS concentration. [b] 1,1-dichloroethylene present at 0.06 M. [c] Mole fraction. [d] Measured solubility, mol L^{-1}. [e] Mole ratio.

Scheme I

$$\text{S}_\sigma \rightleftarrows \text{PI}$$

$$\text{PI} + \text{NBS} \rightarrow \text{BPI} + \text{S}_\sigma$$

$$\text{S}_\sigma + \text{CH}_2\text{Cl}_2 \rightarrow \text{SH} + \cdot\text{CHCl}_2$$

$$\cdot\text{CHCl}_2 + \text{NBS} \rightarrow \text{BrCHCl}_2 + \text{S}_\sigma$$

Although radical-chain substitution and addition reactions can be carried out with *N*-chlorosuccinimide (NCS) and *N*-iodosuccinimide (NIS) both showing the same selectivities as NBS,[1,6] the ring-opening reaction occurs only with NBS in the presence of suitable alkenes and with NIS under iodine-scavenging conditions (in the presence of allene), producing β-iodopropionyl isocyanate; under no circumstances is any β-chloropropionyl isocyanate observed in product mixtures with NCS as the halogenating agent. This puzzling result will be explained in a later section. A number of analogues of these compounds were examined under conditions successful for NBS and NIS ring opening (X_2 scavenger, CH_2Cl_2 solvent). All of these *N*-halo imides show qualitatively similar selectivities in H-abstraction reactions under the halogen-scavenging conditions, but ring-opening reactions are observed only for the reactants in the left-hand column of Table I. The presence of one or more alkyl substituents at the 2- and/or 3-positions of the succinimidyl ring causes an increase in the yield of the corresponding isocyanate. Although no ring opening is observed for NCS or 2,3-Me_2-NCS, 2,2-Me_2-NCS gives a high yield of acyl isocyanate. Also, the 2-Me- and 2,2-Me_2-NBG are the only glutarimides that undergo ring opening, yielding the 4-bromopentanoyl and 4-bromo-4-methylpentanoyl isocyanates, respectively.

A sharp difference in the course of the reactions is observed in the presence or in the absence of molecular bromine. At bromine concentrations greater than 10^{-3} M, no ring opening and a characteristic set of H-abstraction selectivities toward the substrates neopentane and methylene chloride are observed, independent of the bromine concentration.[6,10] If bromine scavengers

(6) Skell, P. S.; Day, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 1951.
(7) Howard, P. B.; Skinner, H. A. *J. Chem. Soc. A* **1966**, 1536.
(8) (a) Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 2172. (b) Dorfman, L. M.; Adams, G. E. National Bureau of Standards Report No. NSRDS-NBS-46, U.S. Government Printing Office, Washington, D.C.
(9) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4997.

Table III. Effect of Changing NBS Concentration[a] (CH_2Cl_2/CCl_4 Solvent, 3,3-Dimethyl-1-butene Substrate (0.41 M))

$CH_2Cl_2/CH_2Cl_2 + CCl_4$[b]	[NBS][c]	1 mmol	1 %	BPI mmol	BPI %	BPI/1[d]
1.00	0.155	0.28	23.5	0.91	76.5	3.25
0.86	0.118	0.35	23.8	1.12	76.2	3.20
0.70	0.068	0.40	27.0	1.08	73.0	2.70
0.51	0.028	0.36	36.2	0.64	63.8	1.76

[a] 2.25 mmol of NBS; all reaction mixtures remained heterogeneous, ensuring constant NBS concentration. [b] Mole fraction. [c] Measured solubility, mol L^{-1}. [d] Mole ratio.

are present, a different set of H-abstraction selectivities is observed, and for the compounds in the left-hand column ring opening becomes the dominant reaction, these observations being independent of the concentration and the reactivity of the bromine scavengers. There is an in-between region, bromine concentration between 0 and 10^{-3} M, in which the transition from one reaction domain to the other occurs.

Effect of Variation in NBS Concentration on Ring Opening. Tables II and III show how this isomerization reaction is affected by a change in NBS concentration: the success of the ring-opening reaction improves with increasing concentration of NBS. The variation in NBS concentration was accomplished by progressive replacement of CH_2Cl_2 by CCl_4 (the solubility of NBS in CCl_4 is 0.005 M). In the presence of neopentane (0.73 M), mixtures of CH_2Cl_2 and CCl_4 provide media for the reaction in which the saturation concentration can be varied between the limits 0.145 and 0.005 M. Given in Table II are the results for a 10-fold change in NBS concentration in the presence of an excess of neopentane. The neopentane concentration was not diminished by more than 5% during any one run. In each experiment 2.25 mmol of NBS and 5.0 mL of CH_2Cl_2–CCl_4 mixture were used. Partial conversion ensured that excess solid NBS was present at all times, thus providing a constant concentration of NBS throughout the reaction. 1,1-Dichloroethylene was present at 0.06 M to scavenge bromine. In the presence of excess neopentane, reducing the concentration of NBS reduces the yield of BPI, favoring instead the formation of brominated substrate and succinimide. This gradual decrease in the BPI/*neo*-$C_5H_{11}Br$ mole ratio is a consequence of the reversible nature of the ring opening for S_σ, which will be dealt with in the section with that title. A decrease in the concentration of NBS, the radical trapping agent, leads to less efficient bromination of PI, favoring H abstraction from neopentane by S_σ.

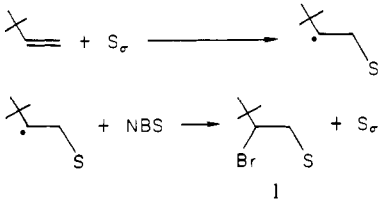
$$S_\sigma + \textit{neo}\text{-}C_5H_{12} \rightarrow SH + \textit{neo}\text{-}C_5H_{11}\cdot$$

$$\textit{neo}\text{-}C_5H_{11}\cdot + NBS \rightarrow \textit{neo}\text{-}C_5H_{11}Br + S_\sigma$$

$$S_\sigma \rightleftarrows PI$$

$$PI + NBS \rightarrow BPI + S_\sigma$$

Bromine-scavenging alkenes also serve as a substrate to which S_σ may add.[11] For example, 3,3-dimethyl-1-butene reacts with S_σ to form the 1-succinimido-3,3-dimethyl-2-butyl radical, which is subsequently trapped by NBS to yield the 1:1 NBS–alkene adduct, **1**, and another S_σ, which continues the chain.

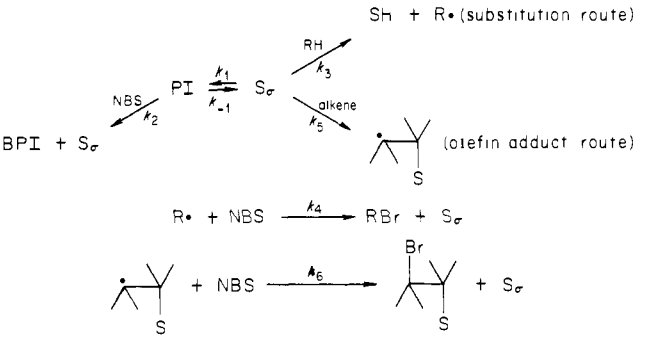


1

(10) A blank experiment showed that β-bromopropionyl isocyanate is not affected by the presence of molecular bromine.

(11) Day, J. C.; Katsaros, M. G.; Kocher, W. D.; Scott, A. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 1950.

Scheme II



Given in Table III are the results for a 5-fold change in NBS concentration in the presence of an excess of 3,3-dimethyl-1-butene (0.41 M). The experimental conditions were identical with those employed for the experiments in Table II except that no 1,1-dichloroethylene was added. Again, partial conversion ensured a constant NBS concentration throughout each reaction. The reversible ring opening of S_σ is, again, responsible for the gradual decrease observed in the BPI/**1** mole ratio. As the concentration of NBS decreases, the open-chain radical PI is trapped less efficiently, allowing the return to S_σ, which adds to the alkene.

Effect of Variation in Alkene Concentration on Ring Opening. Table IV gives the results of a series of experiments in which the concentration of 3,3-dimethyl-1-butene is varied. Reactant mixtures were composed of 1.69 mmol of NBS, 5.0 mL of methylene chloride, neopentane (0.67 M), and various concentrations of 3,3-dimethyl-1-butene (0.029–0.282 M). All reactions were run to 100% consumption of NBS.

In the presence of 3,3-dimethyl-1-butene, the yield of the 1:1 adduct (compound **1**) increases in the expected manner with increasing olefin concentration, thereby reducing the yields of all other products. However, the ratio of BPI to succinimide remains constant, reflecting a constant ratio of ring opening to hydrogen abstraction from the substrates, methylene chloride and neopentane. Further, the rate ratio for hydrogen abstraction from neopentane and methylene chloride, per hydrogen, is constant at the value characteristic for S_σ, 17 ± 2. The value of this rate ratio for S_π is 1.0 ± 0.1 (with molecular bromine present at $>10^{-3}$ M).[1] The different routes for S_σ are summarized in Scheme II. Analysis of the data (vide infra) yields a value of 0.15 ± 0.02 for k_3/k_5, where the k_3 for abstraction refers to (S_σ + neopentane) and the k_5 for addition refers to (S_σ + 3,3-dimethyl-1-butene).

Included in Table IV are results of two additional experiments: one void of Br_2-scavenging alkene and thus containing uncontrolled small amounts of bromine, and the other containing molecular bromine at 0.02 M, which makes the chain carrier S_π and thus gives the rate ratio 1.0 for the neopentane–CH_2Cl_2 competition.[1,6]

The results are consistent with the hypothesis that S_σ is produced without S_π contamination in these bromine-scavenged systems. If mixtures of both S_σ and S_π had been produced in the bromine-scavenged systems, it is reasonable to suppose that the proportions would have been affected by altering the alkene concentrations. Had this been so, the values in the last five columns (Table IV) could not have been constant. Only in the reaction mixture to which neither bromine nor bromine scavenger was added are the results consistent with the intermediacy of a mixture of S_σ and S_π, results attributed to the adventitious development of low concentrations of bromine.

The scavenging of bromine by 3,3-dimethyl-1-butene, ethylene, or 1,1-dichloroethylene produces qualitatively the same effects with one difference: the yields of olefin adduct decrease in this order, reflecting a lower rate for S_σ additions to the latter alkenes.

Effect of Variation of Neopentane Concentration on Ring Opening. Table V shows the results of three experiments in which the neopentane concentration was varied from 0.20 to 0.73 M. In all reactions 1.69 mmol of NBS and 5.0 mL of CH_2Cl_2 were used. 1,1-Dichloroethylene was present at 0.06 M to scavenge bromine. These reactions were carried out to 100% NBS con-

Table IV. Effect of Changing 3,3-Dimethyl-1-butene Concentration[a] (CH_2Cl_2 Solvent, Neopentane Substrate (0.67 M))

	[X=]b	1, %c	BPI, %c	SH/BPId	neo-$C_5H_{11}Br$/BPId	$BrCHCl_2$/BPIe	$(k_{neo\text{-}C_5H_{12}}/k_{CH_2Cl_2})_H$e	k_3/k_5f
S_σ	0.029	2.4	88	0.11	0.089	0.018	17.8	0.145
	0.072	5.5	84	0.12	0.098	0.021	16.8	0.162
	0.144	11	80	0.12	0.096	0.019	18.0	0.155
	0.282	20	71	0.12	0.099	0.022	15.8	0.145
$S_\sigma + S_\pi$	0.0		45	1.2	0.69	0.51	4.8	
S_π	0.0g		0				1.0	

[a] All reactions run to 100% consumption of NBS. [b] Mole liter^{-1}. [c] Absolute yields based on NBS. [d] Mole ratio. [e] On a per hydrogen basis, the rate constant for H abstraction from neo-C_5H_{12} divided by the rate constant for H abstraction from CH_2Cl_2: ([neo-$C_5H_{11}Br$][CH_2Cl_2]/[neo-C_5H_{12}][$BrCHCl_2$])/6. [f] k_3 represents the rate constant for S_σ H abstraction from neopentane, k_5 represents the rate constant for S_σ addition to 3,3-dimethyl-1-butene, k_3/k_5 = [X=][neo-$C_5H_{11}Br$]/[neo-C_5H_{12}][1]. [g] Bromine present at 10^{-2} M.

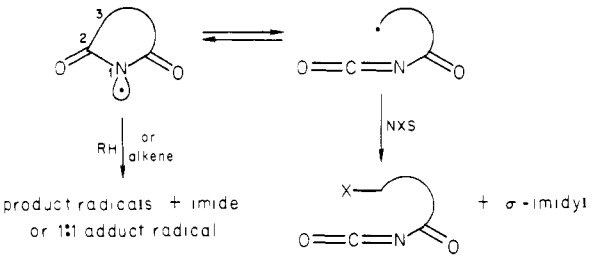
Table V. Effect of Changing Neopentane Concentration[a] (CH_2Cl_2 Solvent, Neopentane Substrate[b])

[neo-C_5H_{12}]c	neo-$C_5H_{11}Br$, %d	$BrCHCl_2$, %d	BPI, %d	$BrCHCl_2$/BPIe	SH/BPIe	$(k_{neo\text{-}C_5H_{12}}/k_{CH_2Cl_2})_H$f
0.20	2.5	2.0	95.5	0.021	0.047	16.3
0.38	4.7	1.9	93.4	0.020	0.071	16.1
0.73	8.3	1.8	89.9	0.020	0.112	15.0

[a] All reactions run to 100% consumption of NBS. [b] 1,1-Dichloroethylene present at 0.06 M. [c] Mole liter^{-1}. [d] Absolute yields based on NBS. [e] Mole ratio. [f] On a per hydrogen basis, the rate constant for H abstraction from neo-C_5H_{12} divided by the rate constant for H abstraction from CH_2Cl_2: ([neo-$C_5H_{11}Br$][CH_2Cl_2]/[neo-C_5H_{12}][$BrCHCl_2$])/6.

version. Increasing the neopentane concentration serves only to increase the yield of neopentyl bromide at the expense of the formation of $BrCHCl_2$ and BPI. Although the SH/BPI mole ratio increases in the expected manner, both the $BrCHCl_2$/BPI mole ratio and the relative rate ratio $(k_{neo\text{-}C_5H_{12}}/k_{CH_2Cl_2})_H$ remain constant at values characteristic for the S_σ chain carrier.

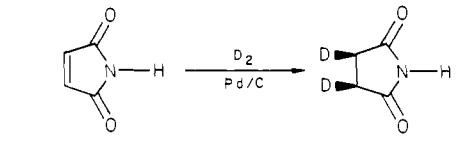
Reversibility of Ring Opening.[2] A full explanation for the observations above is possible with the hypothesis of a rapid, reversible ring opening of the σ form of the imidyl radical.



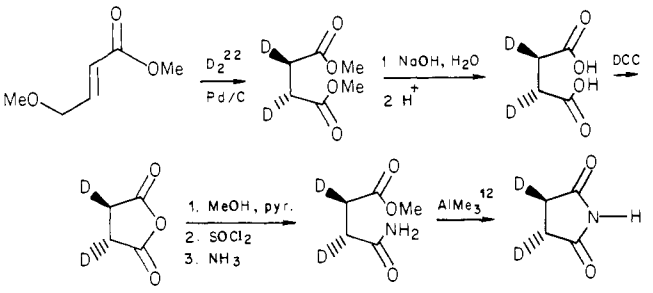
(1) A decrease in concentration of NBS results in a decrease in the rate of trapping of PI, and thus an enhanced diversion of S_σ into additions to alkenes and H-abstraction reactions. (2) NCS reacts less rapidly with PI than NBS, resulting in complete diversion from ring-opened product (see below). (3) *N*-Bromosuccinimides having one or more alkyl substituents at the 2- and/or 3-positions of the ring have an enhanced tendency to undergo ring opening because in the open-chain form they are secondary or tertiary radicals, making less favorable on energetic grounds the return to an S_σ. The return from a tertiary radical to an S_σ is so unfavorable that 2,2-dimethyl-*N*-chlorosuccinimide is the only NCS system that gives ring-opened product. (4) *N*-Haloglutarimidyls, -phthalimidyls, and -hydantoyl have a smaller tendency toward ring-opening reactions, attributable to smaller ring strain or less stable open-chain radicals. The only members of these analogues to exhibit ring opening are the 2-methyl- and 2,2-dimethylglutarimidyls, which open to secondary and tertiary radicals, respectively. These observations imply (a) a smaller rate of ring opening for glutarimidyls than for succinimidyls and (b) an enhanced rate of ring opening with progressive substitution of alkyls at C-2, leading to secondary or tertiary radicals in the open-chain intermediates.

The reversible ring opening was demonstrated conclusively for unsubstituted succinimidyl by studying the reactants *meso*- and *dl*-2,3-dideuterio-*N*-halosuccinimides. Thus it was possible to demonstrate that in NCS reactions which lead only to succinimidyl products (no β-chloropropionyl isocyanate), the succinimidyl radical had equilibrated with the open-chain PI radical.

meso-2,3-Dideuteriosuccinimide (**2**) was prepared by the reaction of maleimide with D_2 gas. Pure *dl*-2,3-dideuteriosuccinimide (**3**) was prepared by the following sequence of reactions:



2



3

Both **2** and **3** were analyzed by mass and infrared spectroscopy. A significant difference in **2** and **3** is observed in the infrared spectra (CHD bend). Compound **2** gives characteristic sharp bands at 700 and 510 cm^{-1}, whereas compound **3** exhibits these bands at 730 and 535 cm^{-1}. The spectra are shown in Figure 1.

With the pure samples available, it was possible to determine the concentration of each component (**2** and **3**) in a diastereoisomerized succinimide sample by quantitative infrared analysis in the CHD bending region. The results of several experiments are shown in Table VI.

Under conditions favorable for NBS isomerization to β-bromopropionyl isocyanate, *meso*-NCS-d_2 and *dl*-NCS-d_2 react to give only chlorinated substrates and diastereoisomerized succinimide (runs A and B). This diastereoisomerization at the 2,3-position in converting NCS to succinimide requires an open-chain intermediate in the chain sequence (Scheme III).

NCS reacts too slowly in trapping PI, thus making H abstraction by S_σ the only pathway to be observed (no β-chloro-

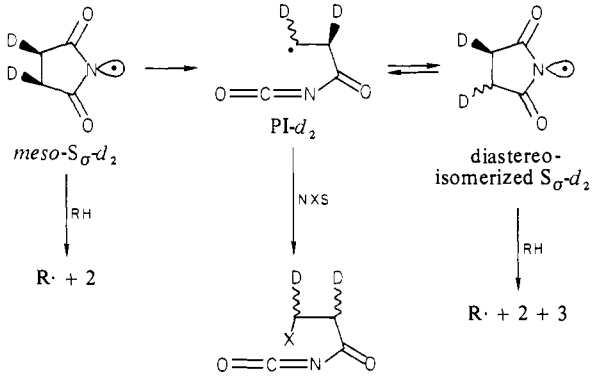
(12) Weinreb, S. M., private communication.

Table VI. Reactions of *meso*- and *dl*-2,3-Dideuterio-*N*-halosuccinimides[a]

run[b]	starting material[c]	added reactants[d]	% isocyanate	recovered succinimide % *meso*	recovered succinimide % *dl*
A	*meso*-NCS-d_2	neopentane, ethylene	0	54	46
B	*dl*-NCS-d_2	neopentane, ethylene	0	45	55
C	*meso*-NBS-d_2	neopentane, ethylene	84	69	31
D	*meso*-NBS-d_2	neopentane, Br_2	0	100	0

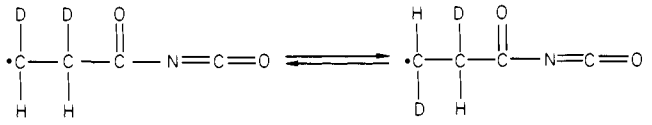
[a] CH_2Cl_2 solvent. [b] Experiments A and D were run twice with identical results. [c] NBS-d_2 (0.22 M), NCS-d_2 (0.29 M). [d] neo-C_5H_{12} (0.73 M), ethylene (0.04 M), Br_2 (0.02 M).

Scheme III

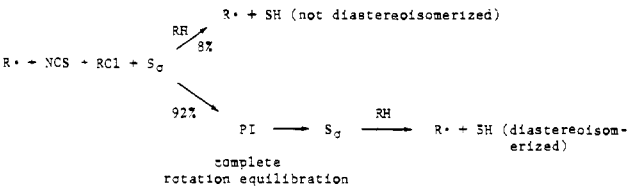


propionyl isocyanate). NBS and NIS compete effectively in trapping the PI intermediate radical, yielding the corresponding acyl isocyanates. The diastereoisomerization observed for the NBS reaction under conditions for isocyanate production (run C) indicates that even in the presence of NBS there is some return to S_σ from the open-chain radical, PI.

To learn whether the deuterium label in PI is totally equilibrated, we converted both the deuterated BPI obtained from the *meso*-NBS-d_2 experiment (run C) and the BPI-d_2 obtained from an additional experiment with *dl*-NBS-d_2 to the corresponding crystalline methyl carbamates by reaction with methanol. The two products were analyzed by ^1H NMR and IR spectroscopy and found to be identical. From this it is clear that rotation equilibration of the open-chain radical is complete. It now becomes possible to give a detailed accounting.



The formation of 46% *dl*-succinimide-d_2 in run A leads to the interpretation that 92% of the succinimide (46% *meso* + 46% *d,l*) is produced by H abstraction from substrate by S_σ radicals which had traversed the PI pathway; 8% *meso*-succinimide-d_2 is obtained from S_σ which had abstracted hydrogen from neopentane or methylene chloride before any ring opening had occurred. The situation is the same (±3%) for the *dl*-NCS-d_2 experiment (run B).



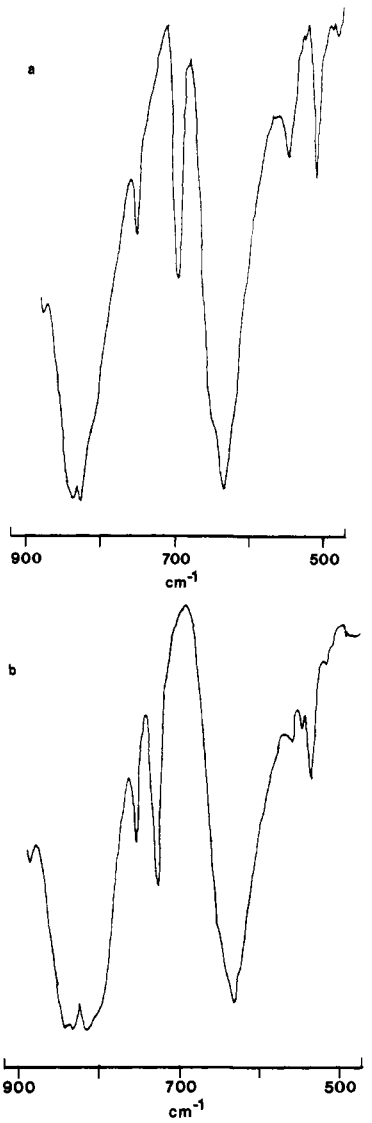
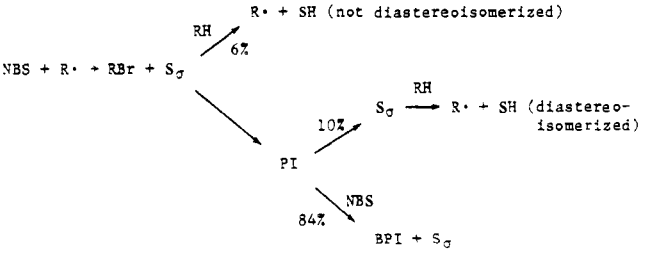


Figure 1. Infrared spectra (CHD bending region) for (a) *meso*-2,3-dideuteriosuccinimide (**2**) and (b) *dl*-2,3-dideuteriosuccinimide (**3**).

The yield of succinimide-d_2 is 16% in the experiment starting with *meso*-NBS-d_2 under S_σ conditions (run C); the remaining 84% of the deuterated bromoimide was found in the product mixture as BPI-d_2. A portion of this succinimide-d_2, 62% (31% *meso* + 31% *dl*), is formed from S_σ which had undergone ring opening and closure prior to H abstraction from substrate: 38% of the succinimide-d_2 (*meso*) results from S_σ which had abstracted hydrogen before isomerization occurred.



These results demonstrate that the fate of the succinimidyl radical produced in the NCS experiments is the same as that produced in the NBS experiments. Ring openings are 12–16 times faster than H abstractions in these experiments.

No isocyanate nor any diastereoisomerization is observed for the *meso*-NBS-d_2 reaction in the presence of 10^{-2} M Br_2 (run D); these are conditions for S_π intermediacy, and ring opening for S_π has not been observed. These observations support the earlier

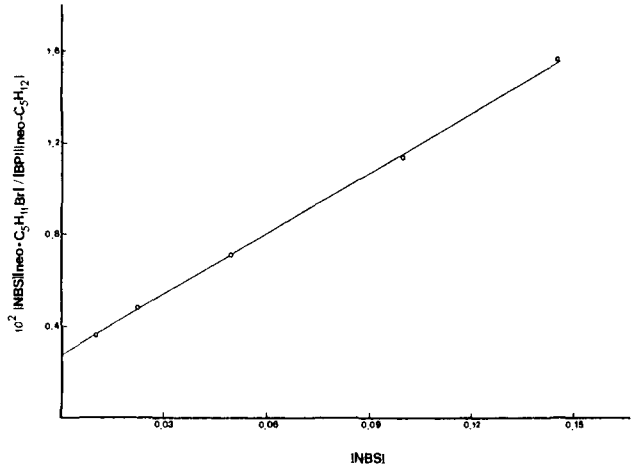


Figure 2. Plot of $[NBS][neo\text{-}C_5H_{11}Br]/[neo\text{-}C_5H_{12}][BPI]$ vs. [NBS] using the data given in Table II for the determination of k_3/k_1 for neopentane and k_{-1}/k_2.

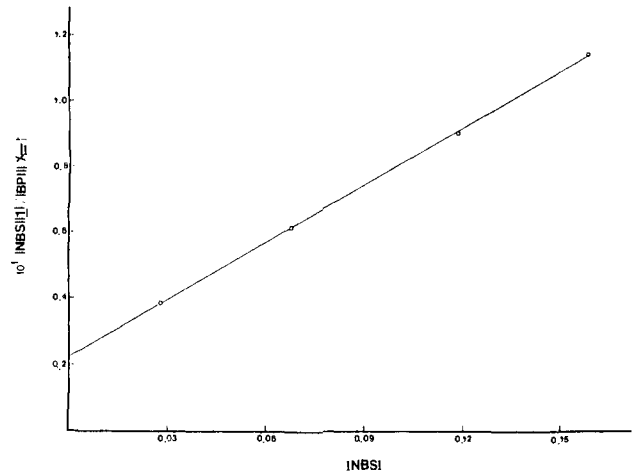


Figure 3. Plot of [NBS][**1**]/[3,3-dimethyl-1-butene][BPI] vs. [NBS] using the data given in Table III for the determination of k_5/k_1 for 3,3-dimethyl-1-butene and k_{-1}/k_2.

conclusion[6] that in the presence of bromine S_π, uncontaminated by S_σ, is the chain carrier.

Kinetic Analysis. The conversion of NBS to BPI in the presence of hydrogen-donating substrate and bromine-scavenging alkene can be described by the following set of reactions:

$$S_\sigma \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PI \xrightarrow[k_2]{NBS} S_\sigma + BPI$$

$$S_\sigma + RH \xrightarrow{k_3} R\cdot + SH$$

$$NBS + R\cdot \xrightarrow{k_4} RBr + S_\sigma$$

$$S_\sigma + \text{alkene} \xrightarrow{k_5} \text{1:1 adduct}\cdot$$

$$NBS + \text{1:1 adduct}\cdot \xrightarrow{k_6} \text{1:1 adduct} + S_\sigma$$

The usual steady-state treatment yields

$$\frac{[NBS][RBr]}{[RH][BPI]} = (k_3/k_1)[NBS] + k_3k_{-1}/k_1k_2 \qquad (3)$$

$$\frac{[NBS][\text{1:1 adduct}]}{[\text{alkene}][BPI]} = (k_5/k_1)[NBS] + k_5k_{-1}/k_1k_2 \qquad (4)$$

Therefore, the ratios k_3/k_1 (H abstraction vs. ring opening), k_5/k_1 (alkene addition vs. ring opening), and k_{-1}/k_2 (ring closure vs. BPI formation) for S_σ can be determined by a plot of the values of the left-hand side in eq 3 and 4 against NBS concentration.

The data given in Tables II and III allow one to utilize eq 3 and 4, since [NBS] remains constant throughout each experiment and the substrates neopentane and 3,3-dimethyl-1-butene are present in large excess. The two plots give straight lines and are shown in Figures 2 and 3.

The rate ratios k_3/k_1 and k_5/k_1 are obtained from the slopes of the graphs, where k_3 refers to S_σ H abstraction from neopentane and k_5 refers to S_σ addition to 3,3-dimethyl-1-butene.

$$k_3/k_1 = 0.087 \pm 0.002 \qquad k_5/k_1 = 0.59 \pm 0.01$$

Combining these two rate ratios gives a value for k_3/k_5 (H abstraction vs. alkene addition). This value is identical with the values obtained by direct competition, listed in Table IV.

$$k_3/k_5 = 0.15 \pm 0.01$$

The rate ratio k_{-1}/k_2 is obtained from the quotient y-intercept/slope for each plot. Values of 0.033 and 0.037 were obtained for this rate ratio.

$$PI \xrightarrow{k_{-1}} S_\sigma$$

$$PI + NBS \xrightarrow{k_2} BPI + S_\sigma$$

$$k_{-1}/k_2 = 0.035 \pm 0.002$$

Since NCS is ineffective in trapping PI, the k_2 for NCS must be at least 50 times smaller than the analogous rate constant for NBS.

$$PI + NCS \xrightarrow{k_2'} CPI + S_\sigma \qquad k_2/k_2' > 50$$

Two more values of the rate ratio, k_3/k_1, for neopentane, can be obtained independently by employing the NCS and NBS data of Table VI (runs A and C). The steady-state treatment for the NCS system yields

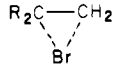
$$k_3/k_1 = \frac{[SH(\text{nondiastereoisomerized})]}{[SH(\text{diastereoisomerized})][neo\text{-}C_5H_{12}]} = 0.11$$

and for the NBS system

$$k_3/k_1 = \frac{[SH(\text{nondiastereoisomerized})]}{([SH(\text{diastereoisomerized})] + [BPI])[neo\text{-}C_5H_{12}]} = 0.089$$

The reasonable agreement in k_3/k_1 rate ratio values for neopentane obtained from the three independent sources gives further credibility to the treatments.

Only one of these rate constants can be independently assigned an approximate absolute value, k_2. If it is assumed that a bimolecular rate constant of 10^{10} L mol^{-1} s^{-1} is correct for primary alkyl radicals reacting with Br_2, then it would follow that k_2 (and k_4) has a value of $\sim 5 \times 10^8$ L mol^{-1} s^{-1}, since Br_2 at concentrations of 10^{-2} M eliminates significant contributions from the reaction of PI or neopentyl radicals with NBS (reaction 2), whereas 10^{-3} M Br_2 allows a small amount of these reactions to occur. Thus it follows that k_{-1} is $\sim 2 \times 10^7$ s^{-1}. Since equilibration of S_σ and PI occurs to a significant extent under all of our S_σ reaction conditions, k_1 must have a value close to that of k_{-1}. Consequently, it follows that k_3 is $\sim 10^6$ L mol^{-1} s^{-1} and k_5 is $\sim 10^7$ L mol^{-1} s^{-1}. An Earlier analogous treatment gave an estimated rate constant $< 10^6$ L mol^{-1} s^{-1} for the reaction of NBS with the bromine-bridged radical:[13]

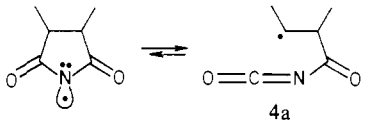


Substituted Succinimidyl Radicals. The 2,3- and 2,2-dimethylsuccinimidyl radicals (**4** and **5**, respectively) were investigated, since opening of the ring under σ-succinimidyl conditions would result in the formation of secondary and tertiary radical intermediates, respectively. Reaction of 2,3-dimethyl-*N*-bromosuccinimide in the presence of neopentane, under conditions in

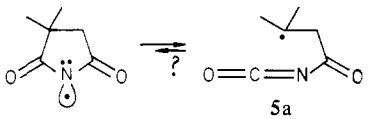
(13) Tuleen, D. L.; Skell, P. S.; Readio, P. D. *J. Am. Chem. Soc.* **1963**, *85*, 2850.

which NBS is converted to BPI in 84% yield (Table IV), produces 3-bromo-2-methylbutanoyl isocyanate in 94% yield. The remaining 6% of the bromoimide is accounted for in the product mixture as 2,3-dimethylsuccinimide, attributed to H abstraction from substrate. Reaction of 2,2-dimethyl-*N*-bromosuccinimide under the identical conditions produces 3-bromo-3-methylbutanoyl isocyanate in 96% yield; the yield of 2,2-dimethylsuccinimide is 4%. The increased yields of isocyanates in these reactions are attributed to the decreasing ability of the PI radical intermediate to undergo ring closure and the increasing rate of conversion of S_σ to PI for the sequence 1°, 2°, 3°, since the rate of H abstraction by a succinimidyl radical should be independent of substitution at the 2-position.

The absence of isocyanate in product mixtures from the reaction of 2,3-dimethyl-*N*-chlorosuccinimide under the same conditions supports the hypothesis of interconversion of **4** and **4a**. The



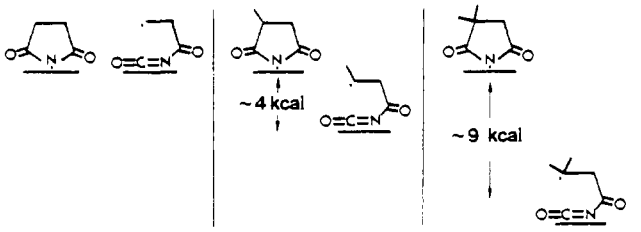
4 4a



5 5a

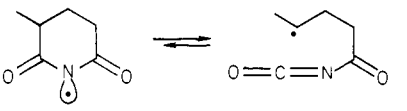
chloroimide reacts too slowly with **4a** for significant trapping of this radical. This expectation could be proven by experiments with *meso*- or *dl*-2,3-dimethyl-*N*-chlorosuccinimides; diastereoisomerized 2,3-dimethylsuccinimide is anticipated. Reaction of 2,2-dimethyl-*N*-chlorosuccinimide under the same conditions, however, produces 3-chloro-3-methylbutanoyl isocyanate in 95% yield. While this experiment demonstrates ring opening for **5**, it is possible that the return to **5** from **5a** does not occur on the trapping time scale available in this experiment.

It had been shown that the relative rates of reactions of radicals with *N*-bromosuccinimides are not altered by alkyl substitutions at C-2 and C-3.[2,14] If one assumes S_σ and PI have the same energy in the case of succinimidyl (to explain the rapid interconversion), an explanation of the behavior of substituted succinimidyls is apparent. For the alkyl-substituted succinimidyls the more stable open-chain secondary and tertiary alkyl radical products make ring opening more favorable and return to the cyclic form less favorable.

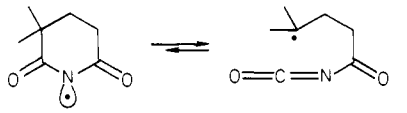


Glutarimidyl Radicals. Earlier it was shown that glutarimidyl and succinimidyl radicals in the σ states show similar behavior in reaction with arenes, alkenes, and alkanes.[6,11]

Glutarimidyl radicals were examined for ring-opening reactions with the expectation that they would be less strained than succinimidyls, and thus be less prone to undergo the isomerization. The observations are consistent with this hypothesis. *N*-Bromoglutarimide and 3,3-dimethyl-*N*-bromoglutarimide do not produce any isocyanates during reactions that involve the corresponding σ-glutarimidyls. However, ring opening to form isocyanate has been observed under σ conditions with 2-methyl-*N*-bromoglutarimide (56%) and 2,2-dimethyl-*N*-bromoglutarimide (94%). In the presence of Br_2 there is no ring opening observed for any of the *N*-bromoglutarimides, only formation of glutarimides and



2-Me-G_σ



2,2-Me_2-G_σ

brominated substrates characteristic of π radicals. This supports the earlier evidence for a π- and σ-glutarimidyl, analogous to S_π and S_σ.[1,6] Again, these observations support the conclusion that alkyl substitution in the 2-position accelerates ring opening. At this time, while it appears that glutarimidyls unsubstituted in the 2-position react with hydrogen-donating substrates without cleavage of the ring, this is not unequivocal (experiments with 2-deuterio substitution are required to settle this point).

Failure of S_π To Ring-Open.[1,6] In halogenations with NBS in CH_2Cl_2 solvent carried out in the presence of bromine scavengers, rearrangement to β-bromopropionyl isocyanate occurs in high yield. In NBS brominations carried out in the presence of Br_2 (10^{-2} M) no rearrangement occurs; only brominated products and succinimide are produced. For NIS iodinations in CH_2Cl_2 in the presence of allene, an efficient I_2 scavenger, one observes β-iodopropionyl isocyanate as the major product. In contrast, for iodinations with NIS in the presence of I_2, no isocyanate is produced. For NBS-Br_2 and NIS-I_2 relative rates of H abstraction for CH_2Cl_2 and neopentane are the same, $[k_{neo\text{-}C_5H_{12}}/k_{CH_2Cl_2}]_H \simeq 1.0 \pm 0.1$, thus implicating an identical succinimidyl radical as the chain carrier in both systems. Likewise, for the three systems NCS–alkene, NBS–alkene, and NIS–allene, the relative rates of H abstraction for neopentane vs. methylene chloride are identical, $[k_{neo\text{-}C_5H_{12}}/k_{CH_2Cl_2}]_H \simeq 17 \pm 2$, again implicating a succinimidyl radical, but a different one from that obtained in the presence of halogens. These are the S_π and S_σ, respectively.

The distinction is striking in the case of 2,2-dimethyl-*N*-bromosuccinimide and 2,2-dimethyl-*N*-bromoglutarimide, which in the absence of Br_2 give large conversions to the corresponding acyl isocyanates, while the production of the acyl isocyanates is totally suppressed by the presence of 10^{-2} M Br_2, H abstraction accounting for 100% of the bromo imide.[2]

Thus, in halo imide systems that can give good conversions to acyl isocyanates, the absence of these isocyanates is a good indicator that S_σ is *not* involved and therefore, conversely, that S_π is the intermediate. In the presence of Br_2 this is an especially impressive argument, since Br_2 is an excellent reagent for trapping the open-chain isocyanatyl radical had any been formed.

Chain Process. Although all the properties of the succinimidyl system discussed above can be rationalized with radical-chain sequences, it was deemed advisable to demonstrate the chain nature of its reactions.

Irradiation at 313 nm[15] of degassed bromine-scavenged reaction systems show an induction period of approximately 5 min; subsequently, the quantum yield for loss of NBS is 63 ± 3 mol einstein^{-1}, the progress of the reaction being followed spectrophotometrically and ultimately by titration of unreacted NBS. If the system is not degassed, the induction period is approximately 20 min. Addition of 2,6-di-*tert*-butyl-*p*-cresol gives complete inhibition. Since no information is available regarding the efficiency of producing noncage radicals, the quantum yield gives a minimum value of chain length.

Photoinitiation with AIBN at 366 nm in degassed bromine-scavenged systems gives a chain length of 30, arrived at by using the yield of 46% noncaged 2-cyanopropyl radicals[16] and assuming

(14) Martin, J. C., private communication.

(15) For NBS in methylene chloride, λ_{max} 274 (ϵ 35), 313 nm (ϵ 10), 366 nm (ϵ = 0).

(16) Hammond, G. S.; Wu, C. H. S.; Trapp, O. D.; Warkentin, J.; Keys, R. T. *J. Am. Chem. Soc.* **1960**, *82*, 5394–5399.

each radical initiates one chain. Consequently, this chain length is a minimum value.

These results are consistent with the following S_σ chain sequence:

$$S_\sigma + RH \rightarrow SH + R\cdot$$

$$R\cdot + NBS \rightarrow RBr + S_\sigma$$

$$S\sigma \rightleftarrows PI$$

$$PI + NBS \rightarrow BPI + S_\sigma$$

The chain character of the S_π reactions was examined by irradiation of Br_2 containing systems (2×10^{-3} M Br_2) at 366 nm for Br_2 dissociation and 313 nm at which two-thirds of the light is absorbed by Br_2 and the remainder by NBS. In both instances the quantum yields were 7–9, with loss of NBS and no loss of Br_2. The identical quantum yields could be coincidence or an indication that both Br_2 and NBS dissociate to noncaged radicals with similar efficiency. The quantum efficiency for escape of Br atoms from the cage, in CCl_4, is 0.22,[27] making the minimum chain length ~35.

$$S_\pi + RH \rightarrow SH + R\cdot$$

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

$$Br\cdot + NBS \rightarrow S_\pi + Br_2$$

With thermal initiation both S_σ and S_π chain lengths of 25–30 are observed.[28]

Concluding Remarks

The succinimidyl radicals produced from reactions of NXS in the presence of halogen show equal reactivity toward the C–H bonds of CH_2Cl_2 and neopentane and do not undergo ring opening. The succinimidyl radicals produced in the halogen-scavenged systems strongly prefer H abstraction from neopentane and undergo extensive ring opening. This different behavior for the succinimidyls produced under the two separate conditions is impossible to explain with a single imidyl radical: while alkene might consume imidyl radicals in addition processes, or X_2 cause return of imidyl radicals to *N*-halo imides, the presence of alkene or halogen cannot affect the competition reactions (additions and H abstractions) and ring openings if the same type of imidyl radical was involved in these two sets of reaction conditions.

We conclude that ground-state S_π is produced with halogen present in the system, generated from the near thermoneutral reaction of NXS + X· (reaction 1). Excited-state S_σ is generated from the exothermic reaction of NXS + 1°R· (reaction 2) when free halogen is absent. Only S_σ undergoes ring opening; S_π does not. The presence of β-bromopropionyl isocyanate in a product mixture may be taken as the identifying signature of a σ-succinimidyl radical.

Experimental Section

General Information. ^{1}H NMR spectra were recorded on either a Varian EM-360 or Bruker WP-200 spectrometer with chemical shifts reported on the δ scale relative to Me_4Si. Infrared analyses were carried out on a Perkin-Elmer 580 or 727 spectrometer. Mass spectra were taken on either a AEI-MS 902 run at 70 eV or a Finnigan 3200 CI (CH_4) at low resolution. Ultraviolet spectra were recorded on either a Cary 17 or Hewlett-Packard 8450 A spectrometer. Gas chromatography analyses were carried out on a Varian 1400 FID with a 60/80 Carbopack B 1% SP-1000 6 ft × 2 mm or a 100/120 Chromosorb Q 10% Silar 10 6 ft × 2 mm column. Melting points were measured on a Thomas-Hoover apparatus and are uncorrected.

Materials. *N*-Bromosuccinimide and *N*-chlorosuccinimide were obtained from Aldrich Chemical Co. and were either recrystallized from water or used as received. *N*-Iodosuccinimide was prepared by the method described by Djerassi and Lenk.[17] A sample of 2,3-dimethylsuccinimide was graciously provided by Dr. J. C. Martin. Other imides and *N*-halo imides were prepared as described. Methylene chloride and carbon tetrachloride were purified by successive extraction with concentrated H_2SO_4, distilled water, and 5% aqueous sodium bicarbonate solution, dried with anhydrous calcium chloride, and distilled from phosphorus pentoxide. Neopentane, Phillips 99%, was used without further purification. 3,3-Dimethyl-1-butene and 1,1-dichloroethylene were obtained from the Aldrich Chemical Co.; the former was used as received and the latter vacuum distilled prior to use. Ethylene, Matheson 99.5%, was used without further purification. Bromine employed in this work was Mallinckrodt Analyzed reagent grade and was used without further purification. 2,6-Di-*tert*-butyl-*p*-cresol, Aldrich Chemical Co., was used as received. 2,2′-Azobisisobutyronitrile, Aldrich Chemical Co., was recrystallized twice from absolute ethanol below 40 °C in subdued light and stored in vacuo in the dark. Authentic samples of neopentyl bromide, neopentyl chloride, and bromodichloromethane were obtained from Pfaltz and Bauer, Inc., Stamford, CT.

2,2-Dimethylsuccinimide was prepared by the method described by Johnson[18] for the preparation of imides using 2,2-dimethylsuccinic acid and ammonium hydroxide (28% NH_3). The imide was used for the preparation of the *N*-bromo derivative without a purification, 94% yield: mp 94–101 °C (lit.[19] mp 105–107 °C); ^{1}H NMR (acetone-d_6) δ 1.2 (s, 6 H), 2.6 (s, 2 H).

2,2-Dimethylglutarimide was prepared in the same manner as the previous reaction with 2,2-dimethylglutaric anhydride and ammonium hydroxide and was used for the preparation of the *N*-bromo derivative without purification, 85% yield: mp 139–144 °C (lit.[20] mp 150 °C); ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 6 H), 1.7 (t, J = 3 Hz, 2 H), 2.5 (t, J = 3 Hz, 2 H), 8.4 (br s, 1 H).

2-Methylglutarimide was prepared by acid hydrolysis of α-methylglutaronitrile (Dupont), subsequent dehydration of the α-methylglutaric acid product with acetic anhydride, and then utilization of the same procedure as the previous reaction, using the 2-methylglutaric anhydride produced. The desired imide was recrystallized from 1:1 benzene–petroleum ether: 60% yield; mp 90–91 °C (lit.[21] mp 91 °C); ^{1}H NMR ($CDCl_3$) δ 1.25 (d, J = 3.5 Hz, 3 H), 1.7–2.05 (m, 2 H), 2.3–2.8 (m, 3 H), 8.5 (br s, 1 H).

***meso*-2,3-Dideuteriosuccinimide** was prepared by the reduction of maleimide (10.06 g, 0.104 mol) with 1 atm of D_2 (Matheson, 99.5%) in 500 mL of 1,2-dimethoxyethane, with 0.5 g of 10% palladium on charcoal catalyst, requiring 10 h for theoretical uptake. The solution was filtered and DME removed in vacuo, leaving a white residue. Recrystallization from absolute ethanol afforded 7.83 g of imide: 75% yield; mp 121–122 °C; ^{1}H NMR (acetone-d_6) δ 2.65 (s, 2 H), 10.0 (br s, 1 H); MS (EI), m/e 101 (M^+) = $C_4H_3D_2NO_2$ (m/e 101:100:99 = 1.0:0.10:0.05), where m/e 99 (M^+) = $C_4H_5NO_2$; IR (KBr) 3170 (m, br), 3080 (m), 2820 (m), 1770 (s), 1715 (s), 1690 (s), 1365 (m), 1290 (w), 1270 (m), 1240 (m), 1190 (s), 1005 (w), 895 (w), 840 (m), 830 (m), 760 (w), 700 (w), 640 (m), 550 (w), 510 (w), 420 (m) cm^{-1}.

***dl*-2,3-Dideuteriosuccinimide** was prepared as follows: *dl*-2,3-Dideuteriosuccinic acid was prepared from dimethyl fumarate to ensure dideuterio incorporation in the reaction with D_2 (the reaction of fumaric acid with D_2 leads to significant amounts of mono- and trideuteriosuccinic acid). Dimethyl fumarate was converted to dimethyl *dl*-2,3-dideuteriosuccinate in the same manner as the previous reaction in ethyl acetate, as described by Childs and Bloch.[22] The liquid product obtained in 97% yield was not further purified. ^{1}H NMR (CCl_4) and IR (neat) spectra were identical with that reported by Childs and Bloch.[22] Saponification with 2 equiv of sodium hydroxide, neutralization, and subsequent continuous extraction with diethyl ether afforded a white solid which was recrystallized from acetonitrile, 89% yield, mp 196 °C (lit.[22] mp 194 °C). Direct conversion of the *dl*-2,3-dideuteriosuccinic acid to the dideuteriosuccinimide by the method described by Johnson[18] afforded diastereoisomerized product, attributed to the high temperature required to decompose the diammonium succinate. An alternate scheme was devised for the synthesis of *dl*-2,3-dideuteriosuccinimide from the corresponding succinic acid.

The acid was dehydrated to the corresponding anhydride with *N*,*N*′-dicyclohexylcarbodiimide (1.8 equiv) in THF at 5 °C. *dl*-2,3-Deuteriosuccinic anhydride was isolated by extraction with ethyl acetate and evaporation of solvent and then recrystallation from absolute ethanol (80% yield) mp 115–117 °C.

The *dl*-2,3-dideuteriosuccinic anhydride (4.0 g, 0.040 mol) was allowed to react with methanol (12.0 mL, 0.280 mol) and pyridine (4.0 mL, 0.050 mol) at room temperature for 0.5 h. Excess methanol and pyridine were removed in vacuo, and thionyl chloride (4.0 mL, 0.056 mol) was added dropwise to the liquid residue at 0 °C. After 0.5 h excess thionyl

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chloride was removed and 40 mL of diethyl ether was added to precipitate pyridinium hydrochloride. The filtrate was added dropwise to ammonia (0.8 mol) in 25 mL of methanol cooled in a dry ice–acetone bath, precipitating ammonium chloride. The excess ammonia, ether, and methanol were evaporated and 70 mL of absolute ethanol was added to dissolve the methyl *dl*-2,3-dideuteriosuccinamate. Evaporation of ethanol in vacuo yielded a white solid, which was recrystallized from benzene: 2.39 g, 45% yield; mp 84 °C; ^{1}H NMR (acetone-d_6) δ 2.55 (s, 2 H), 3.65 (s, 3 H), 5.7 (br s, 2 H).

To the methyl *dl*-2,3-dideuteriosuccinamate (1.60 g, 0.012 mol) in 35 mL of methylene chloride was added 2 M trimethylaluminum in toluene (10.0 mL, 0.020 mol) under N_2 atmosphere. After stirring for 48 h at ambient temperature, 5.0 mL of 5% aqueous hydrochloric acid and 50 mL of chloroform were added. The chloroform layer was dried over Na_2SO_4. Vacuum removal of chloroform left a white solid, which was recrystallized from absolute ethanol, yielding 1.01 g of *dl*-2,3-dideuteriosuccinimide: 83% yield; mp 122 °C; MS (EI), *m/e* 101 (M^+) = $C_4H_3D_2NO_2$ (*m/e* 101:100:99 = 1.0:0.10:0.02) where *m/e* 99 (M^+) = $C_4H_5NO_2$; IR (KBr) 3170 (m,b), 3080 (m), 2820 (m), 1770 (s), 1715 (s), 1690 (s), 1365 (m), 1290 (w), 1270 (m), 1250 (m), 1190 (s), 1005 (w), 840 (m), 830 (m), 760 (w), 730 (w), 640 (m), 535 (w), 420 (m) cm^{-1}.

The following substituted *N*-halosuccinimides were prepared from the corresponding succinimides by using the method described by Pearson and Martin[23] (aqueous sodium bicarbonate and halogen) in 50–85% yield: **2,2-dimethyl-*N*-bromosuccinimide**, mp 155–157 °C, ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 6 H), 2.75 (s, 2 H); **2,2-dimethyl-*N*-chlorosuccinimide**, mp 106–109 °C, ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 6 H), 2.9 (s, 2 H); **2,3-dimethyl-*N*-bromosuccinimide**, mp 86–88 °C, ^{1}H NMR ($CDCl_3$) δ 1.4 (d, J = 4 Hz, 6 H), 2.4–2.9 (m, 2 H); **2,3-dimethyl-*N*-chlorosuccinimide**, mp 54–55 °C, ^{1}H NMR ($CDCl_3$) δ 1.4 (d, J = 4 Hz, 6 H), 2.5–3.0 (m, 2 H).

The dideuterio-*N*-halosuccinimides were prepared from the succinimides by using aqueous sodium hydroxide and halogen, and recrystallization from water, (70–85% yield): ***meso*-2,3-dideuterio-*N*-bromosuccinimide**, mp 177–179 °C; ***meso*-2,3-dideuterio-*N*-chlorosuccinimide**, mp 145–148 °C; and ***dl*-2,3-dideuterio-*N*-bromosuccinimide**, mp 177–179 °C.

The substituted *N*-bromoglutarimides were prepared from the corresponding glutarimides by reaction with acetyl hypobromite[24] (silver acetate and bromine) in Freon 11 (70–80% yield) with no further purification: **2,2-dimethyl-*N*-bromoglutarimide**, mp 70–71 °C, ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 6 H), 1.75 (t, J = 3 Hz, 2 H), 2.85 (t, J = 3 Hz, 2 H), and **2-methyl-*N*-bromoglutarimide**, mp 70–71 °C, ^{1}H NMR ($CDCl_3$) δ 1.35 (d, J = 3.5 Hz, 3 H), 1.75–2.1 (m, 2 H), 2.55–3.05 (m, 3 H).

β-Bromopropionyl isocyanate was prepared by the method of Johnson and Bublitz.[3] Pure β-bromopropionyl isocyanate was also isolated from product mixtures described below by vacuum trap-to-trap distillation (1 mm) at room temperature into a −10 °C trap (ethylene glycol–N_2): ^{1}H NMR ($CDCl_3$) AA′XX′ with triplets at δ 3.05, 3.55 (J = 1, 3 Hz, 4 H); IR (CH_2Cl_2) most prominent band at 2245 (s, –NCO), 1735 (m), 1400 (m), 1070 (m) cm^{-1}.

***N*-(2-Bromo-3,3-dimethyl-1-butyl)succinimide (1)** was isolated from product mixtures described below by (a) removal of volatile materials in vacuo, (b) extraction of nonvolatile products with CCl_4, and (c) evaporation of CCl_4 in vacuo, leaving a white residue. Recrystallization from hexane afforded pure **1**: mp 84–86 °C; ^{1}H NMR (CCl_4) δ 1.1 (s, 9 H), 2.65 (s, 4 H), 3.6–4.4 (m, 3 H); MS (EI), *m/e* 263, 261 (1:1, M^+ = $C_{10}H_{16}NO_2Br$), 206, 204 (1:1, $M^+ - C_4H_9$), 182 (M^+ – Br).

Photolysis Experiments. All reactions were carried out in 30-mL capacity Pyrex pressure tubes sealed with Teflon needle valves. Reactant mixtures were degassed 3 times by a freeze–thaw technique with freezing and evacuation at −196 °C and thawing at ambient temperature. The sealed pressure tube, in a Pyrex water-circulating bath maintained at 14–15 °C, was irradiated (6 in. away) with a 400 W medium-pressure mercury arc while being stirred magnetically.

Typically, the *N*-halo imide and solvent were transferred to the pressure tube and degassed. Neopentane and/or alkene were separately degassed and condensed into the reaction tube, which was then sealed and irradiated. Irradiation times of 0.5–4.0 h were employed. Product yields were obtained from direct ^{1}H NMR integrations employing an internal standard (hexamethyldisiloxane). Yields of brominated substrates were determined relative to an internal standard (chlorobenzene) by gas chromatography, after extraction with 5% aqueous sodium bisulfite, 5% aqueous sodium bicarbonate, and drying with anhydrous sodium sulfate. Products were identified by comparison of GC retention times and/or spectra of authentic samples.

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Reactions Run in the Presence of Halogen Scavengers. Photolysis of *N*-Bromosuccinimide in CH_2Cl_2 in the Presence of 1,1-Dichloroethylene. NBS (1.69 mmol), CH_2Cl_2 (78.1 mmol), and 1,1-dichloroethylene (3.10×10^{-1} mmol) were irradiated for 1.0 h. The initially heterogeneous solution became homogeneous within 15 min; product composition from ^{1}H NMR (CH_2Cl_2): $BrCH_2CH_2C(O)NCO$ (1.65 mmol), $CHBrCl_2$ (4.0×10^{-2} mmol), succinimide (4.0×10^{-2} mmol); IR (CH_2Cl_2) 2245 (s) cm^{-1}.

Photolysis of *N*-Bromosuccinimide in CH_2Cl_2/CCl_4 Mixtures in the Presence of Neopentane and 1,1-Dichloroethylene. NBS (2.25 mmol), CH_2Cl_2 (62.5 mmol), CCl_4 (10.1 mmol), *neo*-C_5H_{12} (4.00 mmol), and 1,1-dichloroethylene (3.10×10^{-1} mmol) were irradiated for 35 min. The solution remained heterogenous throughout the irradiation period; product composition from ^{1}H NMR (CH_2Cl_2): $BrCH_2CH_2C(O)NCO$ (1.44 mmol), $CHBrCl_2$ (2.0×10^{-2} mmol), *neo*-$C_5H_{11}Br$ (1.2×10^{-1} mmol), succinimide (1.4×10^{-1} mmol). The results given in Table II were obtained by using identical procedures with altered proportions of CH_2Cl_2 and CCl_4. Individual NBS solubilities were determined by iodometric titration using the initial reaction compositions.

Photolysis of *N*-Bromosuccinimide in CH_2Cl_2/CCl_4 Mixtures in the Presence of 3,3-Dimethyl-1-butene. NBS (2.25 mmol), CH_2Cl_2 (62.5 mmol), CCl_4 (10.1 mmol), and 3,3-dimethyl-1-butene (2.17 mmol) were irradiated for 15 min. The solution remained heterogeneous throughout the irradiation period; product composition from ^{1}H NMR (CH_2Cl_2): $BrCH_2CH_2C(O)NCO$ (1.12 mmol), *N*-(2-bromo-3,3-dimethyl-1-butyl)succinimide (3.5×10^{-1} mmol). The results given in Table III were obtained by using identical procedures with altered proportions of CH_2Cl_2 and CCl_4. Individual NBS solubilities were determined by iodometric titration using the initial reaction compositions.

Photolysis of *N*-Bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and 3,3-Dimethyl-1-butene. NBS (1.69 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (3.62 mmol), and 3,3-dimethyl-1-butene (1.58×10^{-1}) were irradiated for 1.0 h; product composition from ^{1}H NMR (CH_2Cl_2): $BrCH_2CH_2C(O)NCO$ (1.50 mmol), succinimide (1.6×10^{-1} mmol), *N*-(2-bromo-3,3-dimethyl-1-butyl)succinimide (4.0×10^{-2} mmol); product composition from GC: $CHBrCl_2$ (2.7×10^{-2} mmol), *neo*-$C_5H_{11}Br$ (1.3×10^{-1} mmol). The results given in Table IV were obtained by using identical procedures with the indicated alkene concentration.

Photolysis of *N*-Bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and 1,1-Dichloroethylene. NBS (1.69 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (2.00 mmol), and 1,1-dichloroethylene (3.10×10^{-1} mmol) were irradiated for 1 h. The initially heterogeneous solution become homogeneous within 15 min, product composition from ^{1}H NMR (CH_2Cl_2): $BrCH_2CH_2C(O)NCO$ (1.56 mmol), $CHBrCl_2$ (3.1×10^{-2} mmol), *neo*-$C_5H_{11}Br$ (7.9×10^{-2} mmol), succinimide (1.1×10^{-1} mmol). The results given in Table V were obtained by using identical procedures with the indicated neopentane concentration.

Photolysis of *N*-Chlorosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Ethylene. NCS (2.00 mmol), CH_2Cl_2 (93.7 mmol), *neo*-C_5H_{12} (4.20 mmol), and ethylene (1.0×10^{-1} mmol) were irradiated for 4.0 h; product composition from ^{1}H NMR (CH_2Cl_2): $CHCl_3$ (2.5×10^{-1} mmol), *neo*-$C_5H_{11}Cl$ (1.40 mmol), succinimide (1.65 mmol), *N*-(2-chloro-1-ethyl)succinimide (δ 2.65, s, 4 H; 3.8, m, 4 H; 8.0×10^{-2} mmol); IR (CH_2Cl_2) void of 2245 cm^{-1} (NCO absent).

Photolysis of *N*-Iodosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Allene. NIS (1.20 mmol), CH_2Cl_2 (1.25×10^2 mmol), *neo*-C_5H_{12} (3.90 mmol), and allene (6.0×10^{-1} mmol) were irradiated for 3.0 h; product composition from ^{1}H NMR (CH_2Cl_2): $ICH_2CH_2C(O)NCO$ (δ 3.0–3.45, m, 4 H; 1.16 mmol), succinimide (3.6×10^{-2} mmol); product composition from GC: $CHICl_2$ ($<5.0 \times 10^{-4}$ mmol), *neo*-$C_5H_{11}I$ (3.6×10^{-2} mmol); IR (CH_2Cl_2) 2245 (s) cm^{-1}.

Photolysis of 2,2-Dimethyl-*N*-bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and 1,1-Dichloroethylene. 2,2-DMNBS (1.45 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (4.00 mmol), and 1,1-dichloroethylene (3.1×10^{-1} mmol) were irradiated for 1.0 h; product composition from ^{1}H NMR (CH_2Cl_2): $BrC(CH_3)_2CH_2C(O)NCO$ (δ 1.8, s, 6 H; 3.0, s, 2 H; 1.39 mmol), 2,2-dimethylsuccinimide (6.2×10^{-2} mmol); product composition from GC: CHB rCl_2 (4.6×10^{-2} mmol), *neo*-$C_5H_{11}Br$ (1.6×10^{-2} mmol); IR (CH_2Cl_2) 2245 (s) cm^{-1}.

The 3-bromo-3-methylbutanoyl isocyanate was isolated by vacuum distillation (1 mm) into a −10 °C trap (ethylene glycol–N_2). Reaction with methanol (0.5 mL) afforded methyl *N*-(3-bromo-3-methylbutanoyl)carbamate: mp 83–86 °C; ^{1}H NMR ($CDCl_3$) δ 1.9 (s, 6 H), 3.3 (s, 2 H), 3.75 (s, 3 H), 8.35 (br s, 1 H); MS (CI), *m/e* 238, 240 (1:1, $M^+ + H$), $C_7H_{12}NO_3Br$.

The identical reaction was carried out with 2,2-dimethyl-*N*-chlorosuccinimide, giving a 96% yield of 3-chloro-3-methylbutanoyl isocyanate: ^{1}H NMR (CH_2Cl_2) δ 1.7 (s, 6 H), 2.95 (s, 2 H); IR (CH_2Cl_2) 2245 cm^{-1}(s), attributed to NCO. The isocyanate was isolated as above; reaction with methanol yielded methyl *N*-(3-chloro-3-methylbutanoyl)-

carbamate, mp 71–72 °C; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 3.2 (s, 2 H), 3.75 (s, 3 H), 8.25 (br s, 1 H); MS (CI), *m/e* 193, 195 (3:1, $M^+ + H$) $C_7H_{12}NO_3Cl$.

Photolysis of 2,3-Dimethyl-*N*-bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and 1,1-Dichloroethylene. 2,3-DMNBS (1.45 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (4.00 mmol), and 1,1-dichloroethylene (3.1×10^{-1} mmol) were irradiated for 1.0 h; product composition from ^{1}H NMR (CH_2Cl_2): $BrCH(CH_3)CH(CH_3)C(O)NCO$ (δ 1.3, d, *J* = 4 Hz, 3 H; 1.7, dd, J = 1.4 Hz, 3 H; 2.6–3.0, m, 1 H; 4.0–4.45, m, 1 H; 1.36 mmol), 2,3-dimethylsuccinimide (δ 1.2, d, J = 4 Hz, 6 H; 2.35, m, 2 H; 7.0×10^{-2} mmol); product composition from GC: $CHBrCl_2$ (3.6×10^{-2} mmol), *neo*-$C_5H_{11}Br$ (3.5×10^{-2} mmol); IR (CH_2Cl_2) 2245 (s) cm^{-1}.

The 3-bromo-2-methylbutanoyl isocyanate was isolated as previously described and was allowed to react with methanol (0.5 mL), giving the methyl *N*-(3-bromo-2-methylbutanoyl)carbamate: mp 110–116 °C; ^{1}H NMR ($CDCl_3$) δ 1.3 (d, *J* = 3 Hz, 3 H), 1.75 (d, *J* = 3 Hz, 3 H), 3.3–3.55 (m, 1 H) 3.85 (s, 3 H), 4.2–4.45 (m, 1 H), 8.2 (br s, 1 H); MS (CI), *m/e* 238, 240 (1:1, $M^+ + H$) $C_7H_{12}NO_3Br$.

The identical reaction, void of neopentane, was carried out with 2,3-dimethyl-*N*-chlorosuccinimide, producing only chlorinated solvent ($CHCl_3$) and the corresponding imide: IR (CH_2Cl_2) void of 2245 cm^{-1} (NCO absent).

Photolysis of 2,2-Dimethyl-*N*-bromoglutarimide in CH_2Cl_2 in the Presence of Neopentane and 1,1-Dichloroethylene. 2,2-DMNBG (1.36 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (3.91 mmol), and 1,1-dichloroethylene (3.1×10^{-1} mmol) were irradiated for 1.0 h; product composition from ^{1}H NMR (CH_2Cl_2): $BrC(CH_3)_2CH_2CH_2C(O)NCO$ (δ 1.75, s, 6 H; 2.1, t, *J* = 4 Hz, 2 H; 2.75, t, *J* = 4 Hz, 2 H; 1.28 mmol), 2,2-dimethylglutarimide (8.0×10^{-2} mmol); IR (CH_2Cl_2) 2245 (s) cm^{-1}.

The 4-bromo-4-methylpentanoyl isocyanate was isolated by vacuum distillation (1 mm) into a −10 °C trap. Reaction with methanol (0.5 mL) gave the methyl *N*-(4-bromo-4-methylpentanoyl)carbamate: mp 86–88 °C; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 2.1 (t, *J* = 4 Hz, 2 H), 3.0 (t, *J* = 4 Hz, 2 H), 3.75 (s, 3 H), 8.3 (br s, 1 H); MS (CI), *m/e* 252, 254 (1:1, $M^+ + H$) $C_8H_{14}NO_3Br$.

Photolysis of 2-Methyl-*N*-bromoglutarimide in CH_2Cl_2 in the Presence of Neopentane and 3,3-Dimethyl-1-butene. 2-MNBG (1.56 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (3.88 mmol), and 3,3-dimethyl-1-butene (1.58×10^{-1} mmol) were irradiated for 1.5 h; product composition from ^{1}H NMR (CH_2Cl_2): $BrCH(CH_3)CH_2CH_2C(O)NCO$ (δ 1.7, d, *J* = 3.5 Hz, 3 H; 2.15, t, *J* = 3.5 Hz, 2 H; 2.7, q, *J* = 3.5 Hz, 2 H; 4.1, m, 1 H; 6.8×10^{-1} mmol), 2-methylglutarimide (5.3×10^{-1} mmol), *N*-(2-bromo-3,3-dimethyl-1-butyl)-2-methylglutarimide (δ 1.1, s, 9 H; 4.1, m, 3 H; with imide signals 8.0×10^{-2} mmol), $CHBrCl_2$ (2.5×10^{-1} mmol), *neo*-$C_5H_{11}Br$ (2.8×10^{-1} mmol); IR (CH_2Cl_2) 2245 (s) cm^{-1}.

The 4-bromopentanoyl isocyanate was isolated by vacuum distillation (1 mm) into a −10 °C trap. Reaction with methanol (0.5 mL) gave the methyl *N*-(4-bromopentanoyl)carbamate: mp 86–91 °C; ^{1}H NMR ($CDCl_3$) δ 1.75 (d, *J* = 3 Hz, 3 H), 2.15 (t, *J* = 3 Hz, 2 H), 2.9 (q, *J* = 3 Hz, 2 H), 3.75 (s, 3 H), 4.15 (m, 1 H), 7.65 (br s, 1 H); MS (CI), *m/e* 237, 239 (1:1, $M^+ + H$) $C_7H_{12}NO_3Br$.

Reactions Run in the Presence of Halogen. Photolysis of *N*-Bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Bromine. NBS (1.20 mmol), CH_2Cl_2 (31.2 mmol), *neo*-C_5H_{12} (8.88 mmol), and Br_2 (5.0×10^{-2} mmol) were irradiated for 2.5 h; product composition from ^{1}H NMR (CH_2Cl_2): succinimide, $CHBrCl_2$ (2.1×10^{-1} mmol), *neo*-$C_5H_{11}Br$ (3.7×10^{-1} mmol); IR (CH_2Cl_2) void of 2245 cm^{-1} (NCO absent).

Photolysis of *N*-Iodosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Iodine. NIS (1.20 mmol), CH_2Cl_2 (1.25×10^2 mmol), *neo*-C_5H_{12} (4.00 mmol), and I_2 (4.0×10^{-2} mmol) were irradiated for 3.5 h; product composition from GC: $CHICl_2$ (2.6×10^{-2} mmol), *neo*-$C_5H_{11}I$ (5.4×10^{-3} mmol); IR (CH_2Cl_2) void of 2245 cm^{-1} (NCO absent).

Photolysis of 2,2-Dimethyl-*N*-bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Bromine. 2,2-DMNBS (1.20 mmol), CH_2Cl_2 (62.5 mmol), *neo*-C_5H_{12} (4.00 mmol), and Br_2 (6.3×10^{-2} mmol) were irradiated for 3.0 h; product composition from ^{1}H NMR (CH_2Cl_2): 2,2-dimethylsuccinimide (2.8×10^{-1} mmol), $CHBrCl_2$ (1.7×10^{-1} mmol), *neo*-$C_5H_{11}Br$ (1.1×10^{-1} mmol); Ir (CH_2Cl_2) void of 2245 cm^{-1} (NCO absent).

Photolysis of 2,2-Dimethyl-*N*-bromoglutarimide in CH_2Cl_2 in the Presence of Bromine. 2,2-DMNBG (1.36 mmol), CH_2Cl_2 (78.1 mmol), and Br_2 (1.0×10^{-1} mmol) were irradiated for 2.0 h; product composition from ^{1}H NMR (CH_2CH_2): 2,2-dimethylglutarimide (1.35 mmol), $CHBrCl_2$ (1.35 mmol); IR (CH_2Cl_2) void of 2245 cm^{-1} (NCO absent).

Reactions of 2,3-Dideuterio-*N*-halosuccinimides. For the determination of *dl*- and *meso*-percentage composition in the 2,3-dideuteriosuccinimide products, "solutions" in KBr glasses were prepared by weighing known amounts of pure *dl*- or *meso*-2,3-dideuteriosuccinimide into measured amounts of KBr. Pellets of each were prepared of equal weight (±0.5 mg). The optical densities (at 730 cm^{-1} for *dl*, 700 cm^{-1} for *meso*) vs. concentration gave straight-line plots. The graphs were used to determine the composition of diastereoisomerized samples of 2,3-dideuteriosuccinimides.

Photolysis of *meso*-2,3-Dideuterio-*N*-chlorosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Ethylene. *meso*-2,3-NCS-d_2 (1.47 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (4.00 mmol), and ethylene (2.4×10^{-1} mmol) were irradiated for 5.0 h; product composition from ^{1}H NMR (CH_2Cl_2): succinimide-d_2 (δ 2.65, s, 2 H; 1.22 mmol), $CHCl_3$ (2.0×10^{-1} mmol), *neo*-$C_5H_{11}Cl$ (1.02 mmol); IR (CH_2Cl_2) void of 2245 cm^{-1} (NCO absent). The volatile products were removed by vacuum distillation (1 mm) at ambient temperature. The nonvolatile 2,3-dideuteriosuccinimide was recrystallized twice from absolute ethanol: mp 121 °C; IR (KBr pellet) 760 (w), *730* (*m*), *700* (*m*), 640 (2), 535 (w), 510 (w) cm^{-1}, 54% *meso*- and 46% *dl*-2,3-dideuteriosuccinimides. The identical reaction was run with *dl*-2,3-NCS-d_2, producing 45% *meso*- and 55% *dl*-2,3-dideuteriosuccinimides.

Photolysis of *meso*-2,3-Dideuterio-*N*-bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Ethylene. *meso*-2,3-NBS-d_2 (1.10 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (4.00 mmol), and ethylene (2.0×10^{-1} mmol) were irridated for 2.5 h; product composition from ^{1}H NMR (CH_2Cl_2): $BrCH(D)CH(D)C(O)NCO$ (δ 3.05, br d, 1 H; 3.55, br d, 1 H; 9.24×10^{-1} mmol), succinimide-d_2 (δ 2.65, s, 2 H; 1.76×10^{-1} mmol), $CHBrCl_2$ (2.5×10^{-2} mmol), *neo*-$C_5H_{11}Br$ (1.5×10^{-1} mmol). The volatile products were vacuum distilled (1 mm) at ambient temperature, trapping the 2,3-dideuterio-β-bromopropionyl isocyanate in a −10 °C trap (ethylene glycol–N_2). Reaction with methanol (0.5 mL) yielded the methyl *N*-(2,3-dideuterio-β-bromopropionyl)carbamate, which was recrystallized from methanol: mp 134–136 °C; ^{1}H NMR (acetone-d_6) δ 3.25 (br m, 1 H), 3.65 (br m, 1 H), 3.70 (s, 3 H), 8.9 (br s, 1 H); IR (KBr) 3240 (m), 3165 (m), 3010 (m), 2900 (w), 1790 (m), 1750 (s), 1680 (m), 1510 (s), 1430 (w), 1240 (m), 1210 (s), 1100 (w), 1075 (w), 1060 (w), 1025 (m), 920 (w), 890 (w), 870 (m), 780 (m), 750 (w), 710 (w), 520 (w), 500 (w), 420 (w) cm^{-1}. The nonvolatile 2,3-dideuteriosuccinimide was recrystallized from absolute ethanol: mp 122 °C; IR (KBr pellet) 760 (w), *730* (*m*), *700* (*m*), 640 (s), 535 (w), 510 (m) cm^{-1}; 69% *meso*- and 31% *dl*-2,3-dideuteriosuccinimides.

Photolysis of *dl*-2,3-Dideuterio-*N*-bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Ethylene. *dl*-2,3-NBS-d_2 (1.22 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (4.00 mmol), and ethylene (2.0×10^{-1} mmol) were irradiated for 2.5 h; product composition from ^{1}H NMR (CH_2Cl_2): $BrCH(D)CH(D)C(O)NCO$ (δ 3.05, br d, 1 H; 3.55, br d, 1 H; 1.00 mmol), succinimide-d_2 (δ 2.65, s, 2 H; 1.9×10^{-1} mmol), $CHBrCl_2$ (2.9×10^{-2} mmol), *neo*-$C_5H_{11}Br$ (1.6×10^{-1} mmol). The volatile products were vacuum distilled to isolate the 2,3-dideuterio-β-bromopropionyl isocyanate. Reaction of the isocyanate with methanol (0.5 mL) afforded the methyl *N*-(2,3-dideuterio-β-bromopropionyl)carbamate, which was recrystallized from methanol, mp 134–136 °C. ^{1}H NMR (acetone-d_6) and IR (KBr pellet) were identical with the carbamate produced in the preceding experiment.

Photolysis of *meso*-2,3-Dideuterio-*N*-bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Bromine. *meso*-2,3-NBS-d_2 (1.10 mmol), CH_2Cl_2 (78.1 mmol), *neo*-C_5H_{12} (4.00 mmol), and Br_2 (6.3×10^{-2} mmol) were irradiated for 5.5 h; product composition from ^{1}H NMR (CH_2Cl_2): succinimide-d_2 (δ 2.65, s, 2 H; 1.10 mmol), $CHBrCl_2$ (8.5×10^{-1} mmol), *neo*-$C_5H_{11}Br$ (2.5×10^{-1} mmol); IR (CH_2Cl_2) void of 2245 cm^{-1} (NCO absent). The volatile products were removed by vacuum distillation (1 mm) at ambient temperature. The nonvolatile 2,3-dideuteriosuccinimide product was recrystallized twice from absolute ethanol: mp 122 °C; IR (KBr pellet) 760 (w), *700* (*m*), 640 (s), 510 (w) cm^{-1}; 100% *meso*-2,3-dideuteriosuccinimide.

Chain Lengths. Quantum yield determinations were carried out with a Hanovia 100-W high-pressure mercury arc and an ISA, Inc. monochromator. The light source was standardized by potassium ferrioxalate actinometry following the procedure of Hatchard and Parker.[25] All reactions were carried out in a 1-cm quartz cuvette fused to a 10-mL capacity Pyrex pressure tube, in which reactants were degassed (unless

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(28) Thermal initiation was carried out under conditions similar to the above, at 35 °C, using di-*tert*-butyl peroxyoxalate and 1-bromobutane as substrate. Under S_o conditions a minimum quantum yield of 30 was observed; under S_e conditions (benzene method) the minimum quantum yield is 26. R. L. Tlumak, S. T. Seshadri, and P. S. Skell, submitted for publication.

otherwise indicated), and sealed with a Teflon needle valve. The photolyses were effected without stirring at ambient temperature. The reaction course was followed by withdrawing the cuvette at convenient time intervals and examining spectrophotometrically after thorough agitation. The final concentration of *N*-halo imide was determined by iodometric titration.

Photolysis of *N*-Bromosuccinimide in CH_2Cl_2 in the Presence of 3,3-Dimethyl-1-butene at 313 nm. NBS (5.6×10^{-1} mmol), CH_2Cl_2 (54.6 mmol), and 3,3-dimethyl-1-butene (1.6×10^{-1} mmol) were irradiated for 1.5 h. (a) UV absorbances at λ_{313} (time, min): 1.52 (0), 1.47 (5), 1.27 (10), 1.07 (15), 0.96 (20), 0.79 (30), 0.64 (40), 0.39 (75), 0.32 (90). At 90 min, 18% of NBS remained. $\Phi = 66.7$ mol einstein^{-1}. (b) nondegassed UV absorbances at λ_{313} (time, min): 1.52 (0), 1.52 (5), 1.52 (15), 1.43 (30), 1.24 (45), 1.14 (60), 0.95 (90). At 90 min, 57% of NBS remained. $\Phi = 17.0$ mol einstein^{-1}. (c) in the presence of 2,6-di-*tert*-butyl-*p*-cresol (1.0×10^{-2} mmol), 96% of NBS remained after 90 min (no brominated products).

Photolysis of *N*-Bromosuccinimide in CH_2Cl_2 in the Presence of 3,3-Dimethyl-1-butene and 2,2′-Azobis(isobutyronitrile) at 366 nm. NBS (5.6×10^{-1} mmol), CH_2Cl_2 (54.6 mmol), 3,3-dimethyl-1-butene (1.6×10^{-1} mmol), and AIBN (2.0×10^{-1} mmol) were irradiated for 7.0 h; UV absorbances at λ_{366} (time, min) 0.71 (0), 0.67 (420). At 420 min, 41% of NBS remained with 6% dissociated AIBN. The work of Hammond[16] on the thermal decomposition of AIBN led to a value of 0.46 for the fraction of the total number of AIBN decompositions that yield kinetically "free" radicals. By utilization of this value, in conjunction with the amount of dissociated AIBN and consumed NBS, a chain length of 30 was obtained.

Photolysis of *N*-Bromosuccinimide in CH_2Cl_2 in the Presence of Neopentane and Bromine. NBS (5.6×10^{-1} mmol), CH_2Cl_2 (54.6 mmol), *neo*-C_5H_{12} (2.0 mmol), and Br_2 (6.65×10^{-3} mmol) were irradiated for 2.0 h; (a) At 313 nm, UV absorbances at λ_{313} (time, min): 1.54 (0), 1.53 (5), 1.49 (25), 1.42 (50), 1.25 (95), 1.14 (120). At 120 min, 69% of NBS remained with 0% consumed Br_2. $\Phi = 8.1$ mol einstein^{-1}. (b) At 366 nm, $\Phi = 9.0$ mol einstein^{-1}.

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Registry No. 1, 72323-45-6; **2**, 66633-57-6; **3**, 82621-75-8; NBS, 128-08-5; NIS, 516-12-1; 2,2-Me_2-NCS, 82621-76-9; 2,2-Me_2-NBS, 82621-77-0; 2,3-Me_2-NBS, 82621-78-1; 2-Me-NBG, 82621-79-2; 2,2-Me_2-NBG, 82621-80-5; NCS, 128-09-6; 2,3-Me_2-NCS, 82621-81-6; NCG, 82621-82-7; NBG, 3699-18-1; 3,3-Me_2-NCG, 82621-83-8; 3,3-Me_2-NBG, 66393-63-3; neopentane, 463-82-1; 3,3-dimethyl-1-butene, 558-37-2; 2,2-dimethylsuccinimide, 3437-29-4; 2,2-dimethylglutarimide, 1194-33-8; 2-methylglutarimide, 29553-51-3; *dl*-2,3-dideuteriosuccinic acid, 21156-52-5; *dl*-2,3-dideuteriosuccinic anhydride, 80655-73-8; methyl *dl*-2,3-dideuteriosuccinamate, 82621-84-9; *meso*-2,3-dideuterio-*N*-bromosuccinimide, 66996-78-9; *meso*-2,3-dideuterio-*N*-chlorosuccinimide, 66996-79-0; *dl*-2,3-dideuterio-*N*-bromosuccinimide, 82621-85-0; β-bromopropionyl isocyanate, 18926-24-4; 1,1-dichloroethylene, 75-35-4; ethylene, 74-85-1; allene, 463-49-0; *N*-(2-chloro-1-ethyl)succinimide, 41212-96-8; 3-iodopropanoyl isocyanate, 82621-86-1; 3-bromo-3-methylbutanoyl isocyanate, 82621-87-2; 3-chloro-3-methylbutanoyl isocyanate, 82621-88-3; methyl *N*-(3-chloro-3-methylbutanoyl)carbamate, 82621-89-4; 3-bromo-2-methylbutanoyl isocyanate, 82621-90-7; methyl *N*-(3-bromo-2-methylbutanoyl)carbamate, 82621-91-8; 4-bromo-4-methylpentanoyl isocyanate, 82621-92-9; methyl *N*-(4-bromo-4-methylpentanoyl)carbamate, 82621-93-0; *N*-(2-bromo-3,3-dimethyl-1-butyl)-2-methylglutarimide, 82621-94-1; 4-bromopentanoyl isocyanate, 82621-95-2; methyl *N*-(4-bromopentanoyl)carbamate, 82621-96-3; neopentyl bromide, 630-17-1; neopentyl iodide, 15501-33-4; neopentyl chloride, 753-89-9; 2,3-dideuterio-β-bromopropionyl isocyanate, 82621-97-4; methyl *N*-(2,3-dideuterio-β-bromopropionyl)carbamate, 82638-76-4.

Reactions of a Graded Set of Radicals with *N*-Bromosuccinimide; Two Transition States

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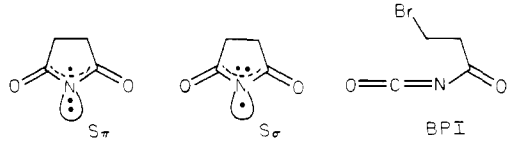
Abstract: The reactions of *N*-bromosuccinimide with a series of radicals have been studied. These reactions fall into two categories, the more reactive radicals producing σ-succinimidyl and the less reactive radicals producing π-succinimidyl. The threshold for the changeover from one reaction domain to the other occurs with radicals less reactive than secondary alkyls. These results are interpreted with two transition states, an in-line transition state for the more reactive radicals and an out-of-plane transition state for the less reactive radicals. An upper limit of 18 kcal/mol is established for the enthalpy difference, $H_{S_\sigma} - H_{S_\pi}$. Two new methods for generating S_π radicals are indicated.

Radical chain reactions in systems containing *N*-bromosuccinimide can be carried out (1) in the presence of Br_2 or (2) in the absence of Br_2 by including small amounts of appropriate bromine-scavenging alkenes.[1,2] With low-reactivity substrates (neopentane, *tert*-butyl chloride, methylene chloride), the substitution of Br for H must be attributed to a hydrogen abstractor that is far more reactive than Br· or R·, thus making succinimidyl(s) (**1** and **2**) the chain carrier(s). The two sets of reaction



1 2 3

conditions described above involve intermediates with distinctly different selectivities in H abstractions for these low-reactivity substrates. Also, in the presence of Br_2, there is no accompanying ring-opening reaction producing β-bromopropionyl isocyanate (BPI, **3**), whereas in the presence of bromine-scavenging alkenes, BPI is the major product.[1-3] These two lines of evidence led to the conclusion that the thermal chain reactions involving succinimidyl radicals operated with either the π or the σ states of the radical, depending only on which reaction (reaction 2 or 3) produced the succinimidyl.[1,2]

with Br_2 present

$$1° \text{ R}\cdot + Br_2 \rightarrow \text{RBr} + \text{Br}\cdot \quad (1)$$

$$\text{Br}\cdot + \text{NBS} \rightarrow Br_2 + S_\pi \quad (2)$$

with Br_2 scavenged

$$1° \text{ R}\cdot + \text{NBS} \rightarrow \text{RBr} + S_\sigma \quad (3)$$

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