Table II. Ferrocyanide Ion Inhibition of the Ferricyanide Oxidation of Heterocyclic Cations at pH 13.0

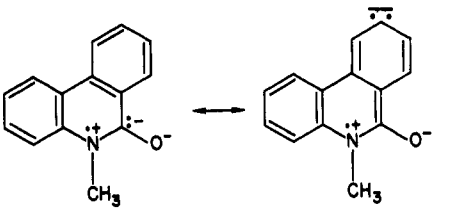
N-methyl cation	k_b/k_{-a} (mol·L^{-1})
pyridinium	[a]
quinolinium	3.5×10^{-4}
isoquinolinium[b]	5.0×10^{-5}
5,6-benzoquinolinium	1.7×10^{-4}
7,8-benzoquinolinium	9.1×10^{-5}
1,10-phenanthrolinium	1.1×10^{-4}
phenanthridinium	1.7×10^{-4}

[a] No significant ferrocyanide inhibition observed. [b] Data from ref 2.

is typical of anilines. Thus the lower reactivity of the quinoline derivative with ferricyanide ion can be traced to the reduced electron density on nitrogen in the quinoline pseudobase.

A comparison of ferrocyanide ion inhibition of the oxidation of these various cations is given in Table II in terms of the value of k_b/k_{-a} at pH 13. This ratio shows no dramatic variation amongst these cations. The relative constancy of this ratio is probably related to the fact that both k_b (base-catalyzed deprotonation of the radical species X) and k_{-a} (electron transfer to X from ferrocyanide ion) are properties of the pseudobase species and are not influenced by considerations of the aromaticities of these cations. The insensitivity of the pyridinium cation oxidations to ferrocyanide ion inhibition can probably be traced to the initial electron transfer to ferricyanide ion being rate-determining throughout the experimentally accessible pH region as a result of the extremely low concentrations of the pseudobase that are attainable in this case.

If the apparent kinetic saturation for k_b/k_{-a} at high pH in Figure 4 is real, it can probably be ascribed to an enhanced stability of the carbanionic charge in Y in this case. The C(6) hydrogen atom of X in the case of the phenanthridinium cation should be much more acidic than for any of the other cations studied since its conjugate base Y (= 1) has benzylic resonance stabilization in addition to the ylidic character common to all other Y species.



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To date we have not investigated substituent effects upon the rates of ferricyanide oxidation of these heterocyclic cations. In the accompanying work we show that it is possible to predict the pH–rate profile for ferricyanide ion oxidation of isoquinolinium cations from the knowledge of pK_{R^+} for the cation of interest. It should be possible to establish analogous substituent effect relationships for any of the heterocyclic cations in the current study.

Acknowledgment. We appreciate the continued support of this work by the Natural Sciences and Engineering Research Council of Canada.

Registry No. *N*-Methylpyridinium, 694-56-4; *N*-ethylpyridinium, 15302-96-2; *N*-methylquinolinium, 21979-19-1; *N*-methylisoquinolinium, 33718-23-9; *N*-methyl-5,6-benzoquinolinium, 33718-26-2; *N*-methyl-7,8-benzoquinolinium, 33496-77-4; 1-methyl-1,10-phenanthrolinium, 48147-04-2; *N*-methylphenanthridinium, 33718-28-4; ferricyanide, 13408-62-3; 1-methyl-2(1*H*)-pyridinone, 694-85-9; 1-ethyl-2(1*H*)-pyridinone, 13337-79-6; 1-methyl-2(1*H*)-quinolinone, 606-43-9; 2-methyl-1-(2*H*)-isoquinolinone, 4594-71-2; 4-methyl-3(4*H*)-benzo[*f*]-quinolinone, 4594-74-5; 1-methyl-2(1*H*)-benzo[*h*]quinolinone, 4594-75-6; 1-methyl-2(1*H*)-1,10-phenanthrolinone, 31535-89-4; 5-methyl-6(5*H*)-phenanthridinone, 4594-73-4.

Glutarimidyl Chemistry: Substitution Reactions. Mechanism of "Ziegler Brominations"

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Glutarimidyl (G·) radicals are generated in liquid-phase chain reactions by halogen atom abstractions from *N*-haloglutarimides by alkyl radicals. These reactions are carried out in the presence of small amounts of alkenes which act as halogen scavengers to eliminate halogen atom chains. The distinguishing characteristics of glutarimidyl radicals are (1) a constant hydrogen abstraction ratio, $(k_{neo\text{-}C_5H_{12}}/k_{CH_2Cl_2})_H = 5.3$ at 15 °C, over a wide range of reaction conditions, (2) no ring opening with glutarimidyls lacking 2-substituents, and (3) ring opening to make 4-bromoalkanoyl isocyanates with *N*-bromoglutarimides substituted by methyl(s) in the 2-position. Glutarimidyl radical hydrogen abstraction selectivities are characterized by early transition states for a variety of substrates, with behavior similar to that shown by chlorine atoms and by succinimidyl radicals. With adequate scavenging of bromine, using 1,3-butadiene or norbornene, brominations of benzylic hydrogen take place with the G· carrier, with selectivities similar to those obtained with Cl·, thus providing *definitive* proof that "Ziegler brominations" are not attributable to G· hydrogen abstractions.

Background

The Ziegler paper[1] describing highly selective allylic (and benzylic) brominations of alkenes with *N*-bromosuccinimide (NBS) in carbon tetrachloride medium was a landmark contribution to synthetic chemistry.[2] After recognition that this was a radical/chain substitution reaction,[3]

(1) Ziegler, K.; Spaeth, A.; Schaaf, E.; Schumann, W.; Winkelmann, E. *Justus Liebigs Ann. Chem.* **1942**, *80*, 551.

(2) Djerassi, C. *Chem. Rev.* **1948**, *43*, 271. Buu Hoi, N. P. *Rec. Chem. Prog.* **1952**, 13, 30. Horner, L.; Winkelmann, E. H. *Angew. Chem.* **1959**, *71*, 349

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3 decades of widespread effort indicated Br· was the *probable* chain carrier.[4] The weakness in this thesis was the failure of all efforts to characterize the chemistry of succinimidyl radical (S·), which some believed might have properties similar to those of Br·.[5] Since identity of the chain carrier depended exclusively on substitution reactions which are not definitive in identifying the hydrogen abstractor, the failure to characterize S· presented a serious flaw in the logic which now is remedied with a description of the analogous reactions of glutarimidyl radicals with benzylic hydrogens.

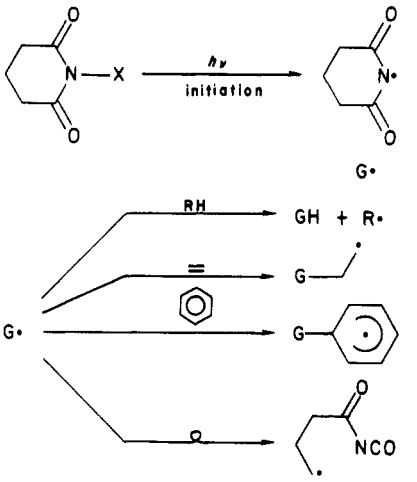
A full panoply of imidyl chemistry, including substitutions on benzylic substrates, became accessible with the recognition of two factors[7] which accentuated the imidyl chain and diminished the importance of the Br· chain. (1) Better solvents increased the concentration of the precursor (NBS) and thus increased the rate of R· + NBS → RBr + S·. Ziegler's insistence on the use of CCl_4 for selective allylic bromination had guaranteed a very low concentration of NBS, thus biasing the system toward the Br· carrier. (2) The use of alkenes (in small amounts) to scavenge Br_2 reduced the rate of R· + Br_2 → RBr + Br·, and this favored the participation of chain carriers other than Br·.

Emphasis on the unexpected properties of the imidyl radicals was eclipsed by a polemic which centered on the possibility of studying the chemistry of both the ground state and a low-lying electronic excited state. Since it is now apparent this possibility has not been explored definitively,[8] we turn our attention to the description of imidyl chemistry, to fully delineate the unanticipated properties of this type of radical.

Glutarimidyl radicals had been the objects of scant attention in the preliminary reports,[6] which recognized, nonetheless, a chemistry analogous to that of succinimidyls.[6,9] Glutarimidyl radicals are readily available by abstraction of a halogen atom from an *N*-chloro- or *N*-bromoglutarimide. The preliminary reports gave indications for the following reactions: additions to alkenes and arenes,[10] nonselective hydrogen abstractions,[6] and ring openings.[9]

The initial studies of imidyl chemistry centered on substitution reactions with NBS, the chemistry of which proved to be complicated by several factors: low solubility of NBS and extensive loss of succinimidyl radicals to ring opening. To a large extent these complications do not occur in glutarimidyl chemistry; the subject of this paper is the substitution chemistry of glutarimidyls.

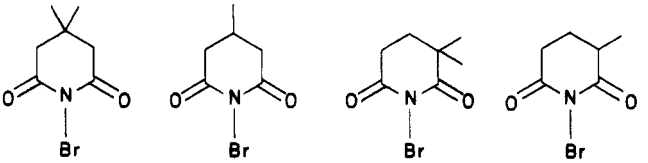
NBS solubilities in nonreactive solvents (Freons, CCl_4)



are extremely low ($<10^{-3}$ M). While the solubility in the reactive solvent methylene chloride is 0.2 M, the addition of nonpolar reactants may reduce this value by a factor of 10 or more. Also succinimidyl radical (S·) chemistry is dominated by a ring-opening reaction which may be the major reaction channel, in some instances as much as 96%. Whereas no combination of substituents on the NBS ring system has been found which eliminates ring opening, this type of reaction occurs only with those glutarimidyl radicals substituted in the 2-position. Appropriate ring substitution of the *N*-bromoglutarimides gives (1) greatly improved solubility characteristics and (2) a control over the rates of ring opening that makes the study of glutarimidyl radicals much simpler.

Results

With either thermal initiation or photoinitiation, glutarimidyl radicals are the major chain carriers in systems consisting of *N*-bromoglutarimide (NBG) or *N*-chloroglutarimide (NCG) in CH_2Cl_2 or $CHCl_3$ solvent. However, the low solubility of NBG in these solvents (0.08 M in CH_2Cl_2; 0.009 M in $CHCl_3$) made unsubstituted NBG less useful as a brominating agent than some of its methyl derivatives. These are all more soluble, but the



33DMNBG 3MNBG 22DMNBG 2MNBG

33DMNBG is the best because (1) it has good solubilities in CH_2Cl_2 and less polar solvents and (2) ring opening is not observed with the 3,3-dimethylglutarimidyl radical. Greater strain in S· may explain this difference between S· and G· behavior.[9] The only reactions observed with 3,3-dimethylglutarimidyl radical are hydrogen abstractions and/or addition reactions. In the presence of alkenes the 2-methyl- or 2,2-dimethylglutarimidyl radicals *do* undergo ring-opening reactions[9] in competition with hydrogen abstractions and additions, but in these latter reactions the selectivities observed are the same as with the 3,3-dimethylglutarimidyl radical.

In the presence of small amounts of alkenes in CH_2Cl_2 solvent, NBG, 3MNBG, or 33DMNBG reacts readily on initiation, yielding exclusively $BrCHCl_2$ and the corresponding glutarimide in equal molar amounts; the alkene precludes a bromine atom chain. An equivalent result is obtained if neopentane is included in the reaction mixture: [$BrCHCl_2$ + neo-$C_5H_{11}Br$] = [glutarimide] (Table I).

(3) Schmid, H.; Karrer, P. *Helv. Chim. Acta* **1946**, *29*, 573. Dauben, H. J.; McCoy, L. L. *J. Am. Chem. Soc.* **1959**, *81*, 4863. *J. Org. Chem.* **1959**, *24*, 1577.

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(5) (a) Dauben, H. J.; Jr.; McCoy, L. J. *J. Am. Chem. Soc.* **1959**, *81*, 5404. (b) Hedaya, E.; Hinman, R. L.; Schomaker, V.; Theodoropulos, S.; Kyle, L. M. *J. Am. Chem. Soc.* **1967**, *89*, 4875.

(6) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381.

(7) Day, J. C.; Lindstrom, M. J.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5616.

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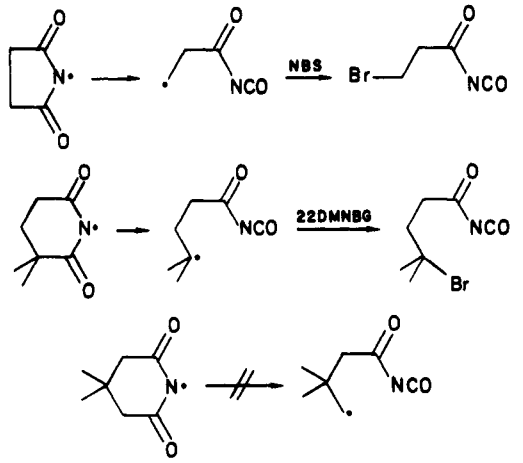

These reactions are sometimes carried out with stirring in the presence of solid NBG to maintain a steady concentration at saturation: the chain lengths for these substitution reactions are 200–300 (calculated from peroxide-catalyzed reactions) and are strongly inhibited by oxygen.

$$\text{NBG} + (CH_3)_4C/(CH_2Cl_2)^{\text{init}} \rightarrow \text{GH} + (CH_3)_3CCH_2Br/(CHBrCl_2)$$

Substitution reactions have been carried out with a variety of substrates, resulting in formation of the corresponding bromides (or chlorides). These substitution selectivities are invariant with alkyl substitution on the NBG ring or with use of the *N*-chloro-3,3-dimethylglutarimide, 33DMNCG. The latter observation *eliminates the possibility that Br· or some species containing Br is the hydrogen abstractor.*

Key observations, summarized in Tables I and II, show competitive halogenations of neopentane and methylene chloride with the following conclusions: regardless of the halogen (*N*-chloro or *N*-bromo) and regardless of the presence or absence of 2- or 3-methyl substituents, the former giving substantial amounts of ring-opened product, the relative rate constants at 15 °C for hydrogen abstractions are the same, $(k_{\text{neo-}C_5H_{12}}/k_{CH_2Cl_2})_H = r(\text{neo-}C_5H_{12}/CH_2Cl_2) = 5.3 \pm 0.1$. This ratio remains unchanged with a 40-fold variation in ratio of substrates (Table III), a twofold change in concentration of substrates (Table IV), variation in concentration of 33DMNBG (Table IV, addition of CCl_4 decreases concentration of 33DMNBG), the particular olefin employed (Table V; see also Tables III and IV), a fourfold change of 1,1-dichloroethene concentrations (Table VI, II, and III), or the mode of initiation (Table VII for peroxide initiation; Tables II–VII for initiation by irradiation). The low olefin concentrations employed in most of these experiments preclude the competitive addition of G· to the olefin as a major reaction. At higher concentrations of alkenes, this addition becomes the major reaction, but there is no change in the relative rates of the hydrogen abstractions. With a 55 °C change in temperature there is a change in selectivity by approximately a factor of 2 (Table VII).

Halogenations of butane and 2,3-dimethylbutane have also been carried out with 33DMNBG and 33DMNCG in the presence of small amounts of alkenes (Tables VIII and IX). On a per hydrogen basis the following reactivity order for G· was found: 3°(18), 2°(6–7), and 1°(≡1). These selectivities were independent of the *N*-halo imide (33DMNBG or 33DMNCG), proving that halogen atom chains make negligible contributions with these substrates. The identical relative rate constants were also found in experiments where both competitions (2°/1°, 3°/1°) were carried out simultaneously. Furthermore, neither the degree of conversion nor the alkene influenced the selectivities.

In Table X the relative rate constants for hydrogen abstractions by a variety of different radicals are sum-

Table I. Comparison of S• and G• Mediated Reactions with Neopentane/CH_2Cl_2 Mixtures Photoinitiated at 15 °C

reactants (mmol)	products (mmol)	r^a(neo-C_5H_{12}/CH_2Cl_2)
NBS (1.69) CH_2Cl_2 (75.0) neo-C_5H_{12} (1.90) CH_2CCl_2 (0.37)	isocyanate (1.56) $CHBrCl_2$ (0.031) neo-$C_5H_{11}Br$ (0.079) succinimide (0.11)	16.8
33DMNBG (1.00) CH_2Cl_2 (78.2) neo-C_5H_{12} (4.10) CH_2CCl_2 (0.51)	$CHBrCl_2$ (0.32) neo-$C_5H_{11}Br$ (0.54) 3,3-dimethylglutarimide (0.88)	5.4
22DMNBG (1.00) CH_2Cl_2 (78.2) neo-C_5H_{12} (4.10) CH_2CCl_2 (0.51)	isocyanate (0.82) $CHBrCl_2$ (0.054) neo-$C_5H_{11}Br$ (0.091) 2,2-dimethylglutarimide (0.15)	5.4

[a] Rate constant ratio calculated on a per H basis.

Table II. Competition of Neopentane/CH_2Cl_2 with Substituted *N*-Haloglutarimides[a] Photoinitiated at 15 °C

N-halo imide	neo-C_5H_{12}/CH_2Cl_2[b]	neo-$C_5H_{11}X$[c]	$CHXCl_2$[c]	r^d(neo-C_5H_{12}/CH_2Cl_2)	%ro[e]
33DMNBG	0.072	0.26	0.11	5.5	0
33DMNCG	0.083	0.018	0.0073	5.0	0
NBG	0.097	0.072	0.024	5.2	0
2MNBG	0.128	0.077	0.019	5.3	56
22DMNBG	0.118	0.060	0.016	5.3	84

[a] Reactions carried out with 0.059 M CH_2CCl_2. [b] Mole ratio. [c] mmol. [d] Rate constant ratio calculated on a per H basis. [e] Ring-opened isocyanate product, (%) based on *N*-halo imide consumed.

Table III. Effect of Substrate Concentration on r^d(Neopentane/CH_2Cl_2) Photoinitiated at 15 °C[a]

neo-C_5H_{12}[b]	neo-C_5H_{12}/CH_2Cl_2[c]	neo-$C_5H_{11}Br$[b]	$CHBrCl_2$[b]	r^d(neo-C_5H_{12}/CH_2Cl_2)
0.422	0.0054	0.09	0.53	5.2
0.62	0.0079	0.11	0.43	5.4
3.85	0.0492	0.21	0.14	5.1
4.04	0.0516	0.28	0.17	5.3
16.67	0.213	0.30	0.045	5.2

[a] 33DMNBG (1.00 mmol) in 5.0 mL of CH_2Cl_2 (78.2 mmol), 1,1-dichloroethene (0.15 M). [b] mmol. [c] Mole ratio. [d] Rate constant ratio calculated on a per H basis.

Scheme I

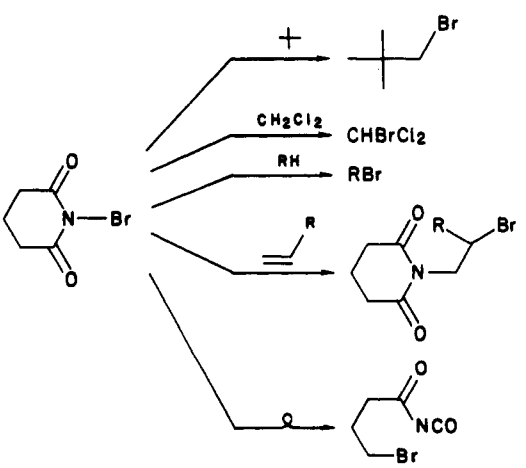

Table IV. Effect of Varying Substrate Concentration on r^f(Neopentane/CH_2Cl_2) Photoinitiated at 15 °C[a]

exp	neo-C_5H_{12}[b]	CH_2Cl_2[b]	neo-C_5H_{12}/CH_2Cl_2[c]	neo-$C_5H_{11}Br$[b]	$CHBrCl_2$[b]	r^f(neo-C_5H_{12}/CH_2Cl_2)
1	5.63	78.2	0.072	0.26	0.11	5.5
2[d]	4.51	62.6	0.072	0.22	0.097	5.3
3[d]	3.33	46.9	0.071	0.36	0.16	5.3
4[d,e]	2.82	39.1	0.072	0.31	0.14	5.1

[a] 33DMNBG (1.00 mmol); 3,3-dimethyl-1-butene (0.095 M). [b] mmol. [c] Mole ratio. [d] CCl_4 was used to make the total volume 5.0 mL. [e] Solubility of 33DMNBG is 0.11 M. [f] Rate constant ratio calculated on a per H basis.

Table V. Effect of Changing the Nature of Olefin on r^d(Neopentane/CH_2Cl_2)[a] Photoinitiated at 15 °C

olefin	neo-C_5H_{12}/CH_2Cl_2[b]	neo-$C_5H_{11}Br$[c]	$CHBrCl_2$[c]	r^d(neo-C_5H_{12}/CH_2Cl_2)
CH_2CCl_2 (0.21 M)	0.060	0.17	0.088	5.4
CH_2CH_2 (0.35 M)	0.062	0.14	0.071	5.3
$(CH_3)_3CCHCH_2$ (0.17 M)	0.066	0.26	0.125	5.3
none	0.065	0.15	0.38	1.0

[a] 33DMNBG (1.00 mmol) in 5.0 mL of CH_2Cl_2. [b] Mole ratio. [c] mmol. [d] Rate constant ratio calculated on a per H basis.

Table VI. Effect of Varying CH_2CCl_2 Concentration on r^e(Neopentane/CH_2Cl_2) Photoinitiated at 15 °C[a]

neo-C_5H_{12}/CH_2Cl_2[b]	$[=<^{Cl}_{Cl}]$[c]	neo-$C_5H_{11}Br$[d]	$CHBrCl_2$[a]	r^e(neo-C_5H_{12}/CH_2Cl_2)
0.051	0.062	0.21	0.12	5.7
0.054	0.165	0.17	0.094	5.6
0.056	0.206	0.13	0.071	5.4
0.054	0.251	0.12	0.071	5.2

[a] 33DMNBG (1.00 mmol) in CH_2Cl_2 (78.2 mmol). [b] Mole ratio. [c] mol/L. [d] mmol. [e] Rate constant ratio calculated on a per H basis.

marized. The abstraction behavior of G· parallels the behavior of Cl·, S·, ·OH, and *t*-BuO· and is distinctly different from that of a methyl radical or a bromine atom.

Discussion

The constant neopentane–methylene chloride halogenation rate constant ratio over a wide range of conditions argues strongly for a common hydrogen abstractor, i.e., a glutarimidyl radical. The competing reactions are summarized in Scheme I.

The failure to perturb the hydrogen abstraction ratios with alterations in concentration or structure of the olefin demonstrates that the alkene plays no role in the hydrogen abstraction step. Hence, the role of alkene is to scavenge Br_2. As long as *the olefin maintains the Br_2 concentration at levels too low to compete with NBG in trapping of radicals, G· is the major chain carrier* in the hydrogen abstraction step. The mechanism shown in Scheme II is consistent with all of these observations. The competition

Scheme II

initiation:	NBG → G·	(1)
propagation:	G· + RH → GH + R·	(2)
	R· + NBG → RBr + G·	(3)

between different substrates is determined in reaction 2.

The hydrogen abstraction selectivities of these G· radicals are remarkable since the relative rates do not always parallel the C–H bond energies (see Table X): neopentane reacts more rapidly even though it has a stronger C–H bond than CH_2Cl_2. Also, the rate constant for G· addition to 3,3-dimethyl-1-butene is only 8× greater than the rate constant, on a per molecule basis, for the abstraction of a hydrogen from neopentane;[20] the corresponding ratio for Cl· is 5, and for S· is 7.[6,9] This failure of G· reactions to follow bond strengths, a characteristic shared by Cl· and S·, is attributed to an early transition state, the energy of which does not depend significantly on the stability of the product radical.[14] The change of selectivity with temperature for this competition is small, corresponding to $\Delta H^{\ddagger}_{\text{neo-}C_5H_{12}} - \Delta H^{\ddagger}_{CH_2Cl_2} = -2.4$ kcal/mol. The major factor determining the rate ratio for neo-C_5H_{12} vs. CH_2Cl_2 may be the electron density in the C–H bond. Since the electron density is diminished by the highly electronegative chloro substituents, the rate of reaction of methylene chloride is decreased relative to neopentane. This contrasts with the ratio of hydrogen abstractions by bromine atoms, r(neo-C_5H_{12}/CH_2Cl_2) = 0.06, which reflects the predominate effect of bond strengths in a later transition state.[14]

Bromination of Benzylic Systems with G·. If the substrate has weak C–H bonds, resulting in a high rate of reaction with Br· atoms (e.g., allylic hydrogens of cyclohexene or benzylic hydrogens), then the alkenes used in Table V do not reduce the concentration of bromine to a value sufficiently low to preclude Br· chains. In the presence of these alkenes Br· chemistry dominates and G· chemistry is not apparent, just as was reported for NBS in the absence of bromine scavengers.[4c-e] But, *with the better bromine scavengers, butadiene or norbornene, the different chemistry, attributable to G·, becomes apparent.*

The competitive substrates used for these experiments were ethylbenzene and toluene, with r defined as (k_{PhEt}/k_{PhMe}) × 1.5, comparing the CH_2 of ethylbenzene and the CH_3 of toluene.

Table VII. Effect of Temperature Variation on r^a(Neopentane/CH_2Cl_2)[b]

temp, °C	33DMNBG[c]	neo-C_5H_{12}[c]	neo-$C_5H_{11}Br$[c]	$CHBrCl_2$[c]	r^a(neo-C_5H_{12}/CH_2Cl_2)
14[d]	0.94	4.2	0.123	0.070	5.4
14[d]	0.87	2.8	0.076	0.064	5.5
14[d]	0.94	3.0	0.105	0.084	5.4
15[d]	0.96	2.55	0.126	0.120	5.4
35[d]	0.79	3.1	0.086	0.085	4.2
35[e]	1.01	2.5	0.151	0.178	4.4
70[d]	1.01	3.1	0.118	0.178	2.8
70[d]	0.84	2.9	0.062	0.098	2.8

[a] Rate constant ratio calculated on a per hydrogen basis. [b] Reaction in 5 mL (78 mmol) of CH_2Cl_2 containing 0.39 mmol of 3,3-dimethyl-1-butene. [c] mmol. [d] Photoinitiated through Pyrex with 450-W medium pressure Hg lamp. [e] Thermal initiation with 0.0085 mmol of di-*tert*-butyl peroxyoxalate, 2 h. [f] $\Delta\Delta H^{\ddagger}$ = 10.0 KJ/mol(−2.4 kcal/mol); $\Delta\Delta S$ = −21 J/mol·K(−5 cal/mol·K).

Table VIII. Photohalogenation of Butane at 15 °C

starting materials[a]		product		$k(2°/1°)_H$[b]
	mmol		mmol	
33DMNCG	0.94	1-chlorobutane	0.047	6.4
3,3-dimethyl-1-butene	0.56	2-chlorobutane	0.20	
butane	3.7			
33DMNBG	0.88	1-bromobutane	0.12	6.1
3,3-dimethyl-1-butene	0.56	2-bromobutane	0.49	
butane	3.3			
33DMNBG	0.94	1-bromobutane	0.042	6.4
3,3-dimethyl-1-butene	1.16	2-bromobutane	0.180	
butane	6.4			

[a] In 5 mL of CH_2Cl_2. [b] Relative rate constant on a per hydrogen basis. [c] 7.7 mmol of 2,3-dimethylbutane was also present (see Table X).

The value r = 20–30 has been reported for NBS alone,[4c-e] and we obtain values within this range from: (a) Br_2/K_2CO_3, (b) Br_2/NBS, (c) Br_2/NBG, (d) 33DMNBG/1,1-dichloroethene, and (e) 33DMNBG/3,3-dimethyl-1-butene. Thus, this is probably Br· chain chemistry, unperturbed by the bromo imides and unperturbed by HBr since in some of these experiments it is efficiently scavenged. It is important to note that under these conditions ethylbenzene undergoes bromination exclusively at the benzylic position.

However, if norbornene or 1,3-butadiene is present as the Br_2-scavenging alkene, although additions to the alkenes are the major reactions, a totally different substitution selectivity pattern is observed for these benzylic substrates. In Table XI two typical experiments are described. In four such experiments the values of r: 3.0, 2.7, 2.7, and 2.7. We attribute this selectivity to G·. Further, with these G· conditions there is substantial reaction at the *unactivated methyl group* of ethylbenzene: the "activated" methyl of toluene is only 2.3× as reactive as the "unactivated" methyl group of ethylbenzene, behavior reminiscent of Cl·. Bromination of ethylbenzene with *N*-bromoglutarimides in the presence of norbornene or 1,3-butadiene results in 25% substitution at the methyl group and 75% at the methylene. Chlorination (with Cl_2) of dilute ethylbenzene in CCl_4 solvent results in 33% reaction at the methyl group and 67% at the methylene.[21]

These lines of evidence point to G· as the major chain carrier in benzylic systems when norbornene or 1,3-butadiene is present. With less efficient bromine scavengers these benzylic systems exhibit a very high susceptibility for reaction with bromine atoms, thus accounting for earlier failure to find reactions of any chain carrier other than Br·.

Two factors may account for the difference in bromine scavenging required to eliminate bromine atom chains for more and less susceptible substrates: (1) with less reactive substrates, the rate of hydrogen abstraction by Br· is relatively slower than with imidyls and (2) with the weaker R· (from substrates with weak C–H bonds) the trapping by NBG is selectively retarded relative to the trapping by Br_2.

Since it is now demonstrated that G· has selectivities distinctively different from Br·, further support is given to the earlier conclusions[4] that the carrier is Br· in Ziegler brominations.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a Varian EM-360, Bruker WH-200, or Bruker WM-360 spectrometer with chemical shifts reported on the δ scale relative to hexamethyldisiloxane (δ = 0.07). Infrared analyses were recorded on a Perkin-Elmer 727 spectrometer with polystyrene standard. Mass spectra were recorded on a Kratos 9/50 spectrometer. Gas chromatographic analyses were performed on a Varian 1200 FID, Varian 1400 FID, or Hewlett Packard HP5790A FID instrument with a Hewlett Packard 3390A integrator equipped with a 60/80 Carbopack B 1% Sp-1000 6 m × 2 mm, a 100/200 Chromosorb δ 10% Silar H 6 m × 2 mm column or a DB-5 capillary column 30 m × 0.32 mm.

Materials. Methylene chloride and carbon tetrachloride were each purified by successive extractions with concentrated H_2SO_4, distilled H_2O, and 5% aqueous sodium bicarbonate solution, drying with anhydrous calcium chloride, and distillation from phosphorus pentoxide. Neopentane, Phillips 99%, was used without further purification. 3,3-Dimethyl-1-butene and 1,1-

Table IX. Photohalogenation of 2,3-Dimethylbutane at 15 °C

NXG[a,b]	alkene[a]	2,3-dimethylbutane[a]	conversn[i]	1-halo-2,3-dimethylbutane[a]	2-halo-2,3-dimethylbutane[a]	$k(3°/1°)_H$[j]
0.92[c]	1.25[e]	7.7	<5	0.0034	0.0114	20
0.92[c]	1.09[f]	7.7	100	0.096	0.289	18
0.97[c]	0.39[g]	7.7	8	~0.003	~0.009	18
1.00[c]	0.78[g]	7.7	27	0.035	0.102	17
0.97[c]	0.39[g]	7.7	38	0.052	0.161	19
0.97[c]	0.39[g]	7.7	63	~0.11	~0.32	18
0.94[c,h]	1.16[g]	7.7	100	~0.08	~0.24	18
0.75[d]	0.45[g]	15.6	?	0.095	0.26	16

[a] mmol. [b] In 5 mL of CH_2Cl_2. [c] 33DMNBG. [d] 33DMNCG. [e] 1,1-Dichloroethene. [f] Vinyl acetate. [g] 3,3-Dimethyl-1-butene. [h] 6.4 mmol of butane were also present (see Table IX). [i] %. [j] Relative rate constant on a per hydrogen basis, directly calculated from GC integrator printout.

Table X. Comparison of Relative Rate Constants of H-Abstractions from Different Substrates for a Variety of Radicals R·[d]

		substrate (bond energy, kcal/mol)				
R· bond energy (kcal/mol)	T[d]	CH_2Cl_2 (99)[b]	1° (98–103)	2° (95)	3° (92)	ref 11
Cl·	−78		1	9	50	12
Cl·	25	0.02[c]	1	3.6	4.2	13
S·	15	0.06	1	4.6[e]	14	14
G·	15	0.19	1	6–7	18	this work
HO·	25		1	7.0	45	15
t-BuO·	20		1	9.2	54	16
Me·	−78		1	200	13000	17
Br·	−78		1	18000	10^7	18
Br·	27	10	1	750	$1.5 \cdot 10^5$	12

[a] °C. [b] Reference 19. [c] Reference 12. [d] On a per hydrogen basis. [e] Reference 8.

Table XI. Competitive Bromination: Ethylbenzene/Toluene with G• in Presence of Norbornene or 1,3-Butadiene Photoinitiated, 15 °C[b]

reactants	products (mmol)	$r^a(C_6H_5CH_2CH_3/C_6H_5CH_3)$
33DMNBG (0.90 mmol)	$C_6H_5CH_2Br$ (0.0082)	3.0
CH_2Cl_2 (78.3 mmol, 13 M)	$C_6H_5CHBrCH_3$ (0.0143)	
$C_6H_5CH_3$ (4.71 mmol, 0.78 M)	$C_6H_5CH_2CH_2Br$ (0.0028)[c]	
$C_6H_5CH_2CH_3$ (4.07 mmol, 0.68 M)	3,3-dimethylglutarimide (0.018)	
1,3-butadiene (3.6 mmol, 0.60 M)	butadiene adducts (0.497)	
33DMNBG (0.90 mmol)	$C_6H_5CH_2Br$ (0.0083)	2.6
CH_2Cl_2 (78.3 mmol, 13 M)	$C_6H_5CHBrCH_3$ (0.0126)	
$C_6H_5CH_3$ (4.71 mmol, 0.78 M)	$C_6H_5CH_2CH_2Br$ (0.0033)[c]	
$C_6H_5CH_2CH_3$ (4.07 mmol, 0.68 M)		
norbornene (2.86 mmol, 0.47 M)		

[a] Rate constant ratio for reactions at CH_2 of ethylbenzene and CH_3 of toluene on a per H basis. [b] Medium pressure 400-W mercury arc through several layers of Pyrex. [c] For comparison of the *methyl* groups of toluene and ethylbenzene with G•: r = 2.5, 2.2 for (toluene/ethylbenzene).

dichloroethene (both Aldrich) were each vacuum distilled prior to use. To remove the inhibitor from the latter the commercial material was distilled at atmospheric pressure, taking only a middle cut.

2,2-Dimethylglutarimide.[22] To 0.04 mol of 2,2-dimethylglutaric anhydride was added 0.085 mol of 28% NH_4OH slowly with stirring at 0 °C. The reaction mixture was then heated to 100 °C to expel H_2O and NH_3. Distillation of the resultant oil at 30-mm pressure yielded a fraction at 95–100 °C. Recrystallization with 95% ethanol resulted in white crystals, 55% yield, mp 169–170 °C (172 °C lit[23]): ^1H NMR ($CDCl_3$, δ) 1.15 (s, 6 H), 1.70 (t, 2 H, J = 3 Hz), 2.45 (t, 2 H, J = 3 Hz), 8.40 (br, s, 1 H); IR (CH_2Cl_2, cm^{-1}) 3170 (m), 3100 (s), 2900 (s), 1730 (s), 1400 (s), 1290 (m), 1150 (s).

2-Methylglutarimide was prepared by the acid hydrolysis of 2-methylglutaronitrile (Dupont), subsequent dehydration of the 2-methylglutaric acid product with acetic anhydride to make 2-methylglutaric anhydride, and the same procedure as above to obtain the imide. Recrystallization from benzene–petroleum ether (1:1) yielded white crystals, mp 90–91 °C: ^1H NMR ($CDCl_3$, δ) 1.25 (d, 3 H, J = 3.5 Hz), 1.7–2.1 (m, 2 H), 2.3–2.85 (m, 3 H), 8.5 (br s, 1 H); IR (CH_2Cl_2, cm^{-1}) 3170 (m), 3050 (s), 2910 (m), 1730 (s), 1410 (s), 1290 (s), 1150 (s).

Glutarimide, 3-methylglutarimide, and 3,3-dimethylglutarimide were obtained from Aldrich Chemical Company and used without further purification.

***N*-Bromo-2,2-dimethylglutarimide.**[24] To 0.02 mol of CH_3COOAg in 50 mL of fluorotrichloromethane was added 0.02 mol of Br_2 in 25 mL of fluorotrichloromethane, at 0 °C over a period of 30 min with stirring. The yellow reaction mixture was filtered through a coarse frit into a Schlenk flask cooled to −78 °C. 2,2-Dimethylglutarimide (0.12 mmol) was added to the solution, and the reaction mixture was stirred for an additional 45 min at room temperature. Removal of the volatiles in vacuo left white crystals, 99% yield, mp 75–76 °C, 99.5% active Br by iodimetry: MS (EI), m/e 221, 219 ($M^+ = C_7H_{10}O_2NBr$), 176, 141, 97, 69, 56; ^1H NMR ($CDCl_3$, δ), 1.25 (s, 6 H), 1.75 (t, 2 H, J = 3 Hz), 2.89 (t, 2 H, J = 3 Hz).

***N*-Bromo-2-methylglutarimide**, prepared by the above method, mp 71 °C: ^1H NMR ($CDCl_3$, δ) 1.35 (d, 3 H, J = 3.5 Hz), 1.75–2.15 (m, 2 H), 2.6–3.05 (m, 3 H).

***N*-Bromoglutarimide**, prepared by the above method, mp 174 °C: ^1H NMR (CH_2Cl_2, δ) 2.10–2.20 (m, 2 H), 2.90 (t, 4 H, J = 3 Hz); MS (EI), m/e 193, 191 ($M^+ = C_5H_6NO_2Br$), 113, 80, 70, 56.

***N*-Bromo-3,3-dimethylglutarimide** was prepared as follows:[25] to a cold solution (0 °C) of 0.06 mol of NaOH in 50 mL of H_2O was added 0.05 mol of 3,3-dimethylglutarimide with stirring until all the imide dissolved. To this mixture was slowly added Br_2 (0.05 mol) via a dropping funnel. The yellow-white precipitate formed was allowed to stir for 30 min prior to filtration. Drying the solid residue under vacuum resulted in white crystals which were recrystallized from CH_2Cl_2 after adding pentane, yield 95%, mp 141–143 °C, extent of bromination 99.8%: ^1H NMR ($CDCl_3$, δ) 1.15 (s, 6 H), 2.70 (s, 4 H); MS (EI), m/e 221, 219 ($M^+ = C_7H_{10}O_2NBr$), 160, 141, 112, 83, 70, 56.

***N*-Chloro-3,3-dimethylglutarimide** was prepared as follows: to a cold solution (0 °C) of 12.5 mmol of NaOH in 50 mL of H_2O was added 12.0 mmol of 3,3-dimethylglutarimide. Cl_2 (~14 mmol) was bubbled into the reaction mixture over a period of 20 min. After having been stirred for 30 min, the reaction products were filtered and vacuum dried (1 torr) to yield white crystals, which were crystallized from CH_2Cl_2 by addition of pentane, yield 85%, mp 94–95 °C, extent of chlorination 99.2%: ^1H NMR ($CDCl_3$, δ) 1.15 (s, 6 H), 2.72 (s, 4 H).

Di-*tert*-butyl Peroxyoxalate.[26] A solution (0.012 mmol) of oxalyl chloride in 40 mL of anhydrous pentane was added dropwise to a stirred cold solution of 2.60 g of pyridine and 2.24 g of *tert*-butyl hydroperoxide in 30 mL of pentane. During the addition, the temperature of the solution was slowly allowed to warm to room temperature, and the pyridinium chloride was then filtered. The filtrate was cooled in a dry ice–acetone bath to yield fine white crystals. The peroxy ester was filtered without delay through a frit kept at −78 °C, and the residue was quickly dissolved in 20 mL of cold CH_2Cl_2 and stored at 0 °C until future use. Care was taken to avoid disturbance to the crystals. Yield 60% (iodometric). The peroxide was dissolved in CH_2Cl_2 and shaken with a $FeSO_4$-solution to reduce remaining *tert*-butyl hydroperoxide, washed with water and dried over molecular sieves. The concentration of the di-*tert*-butyl peroxyoxalate was determined by NMR (δ = 1.34).

4-Bromo-4-methylpentanoyl isocyanate was isolated from the reaction of 22DMNBG with CH_2Cl_2 in the presence of 3,3-dimethyl-1-butene by a vacuum trap-to-trap distillation (1 torr) into a −16 °C trap: ^1H NMR (neat, δ) 1.75 (s, 6 H), 2.15 (t, 2 H, J = 4 Hz), 2.75 (t, 2 H, J = 4 Hz); IR (CH_2Cl_2, cm^{-1}) most prominent band at 2250 (s, NCO), 1740 (m), 1400 (m), 1065 (m), detection limit 0.006 mmol. Reaction of the isocyanate with methanol gives methyl *N*-(4-bromo-4-methylpentanoyl)carbamate, mp 91 °C: ^1H NMR ($CDCl_3$, δ) 1.75 (s, 6 H), 2.15 (t, 2 H, J = 4 Hz), 3.0 (t, 2 H, J = 4 Hz), 3.75 (s, 3 H), 8.3 (br, 1 H).

4-Bromopentanoyl isocyanate was isolated from the reaction of 2MNBG with CH_2Cl_2 in the presence of 3,3-dimethyl-1-butene by a vacuum trap-to-trap distillation (1 torr) into a −16 °C trap:

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^{1}H NMR ($CDCl_3$, δ) 1.70 (d, 3 H, J = 3 Hz), 2.18 (t, 2 H, J = 3 Hz), 2.75 (q, 2 H, J = 3 Hz), 4.20 (m, 1 H). Reaction of the isocyanate with methanol gives methyl *N*-(4-bromopentanoyl)-carbamate: mp 94–96 °C, ^{1}H NMR ($CDCl_3$, δ) 1.75 (d, 3 H, J = 3 Hz), 2.30 (t, 2 H, J = 3 Hz), 2.95 (q, 2 H, J = 3 Hz), 3.75 (s, 3 H), 4.20 (m, 1 H), 8.1 (br, 1 H).

Competition Reactions. All reactions were carried out in 30-mL-capacity Pyrex pressure tubes containing Teflon-coated stir bars, sealed with o-ringed Teflon needle valves. Reactant mixtures were degassed 2–5 times by a freeze–pump–thaw technique with freezing and evacuating at −196 °C and thawing at room temperature. The sealed pressure tube was placed in a temperature-controlled water bath for either peroxide or light initiation. Irradiation was through two layers of Pyrex with a 400-W medium pressure mercury arc at a distance of 5–15 cm, for 0.75–5 h (reaction at 15 °C).

At the completion of a reaction, the volatile materials were separated from the nonvolatiles by high vacuum trap-to-trap distillation. The nonvolatiles were examined by ^{1}H NMR, and the product yields were obtained by direct integrations employing an internal standard (hexamethyldisiloxane). The amount of unreacted *N*-halo imide was also determined iodometrically with an aliquot of the nonvolatiles. The volatile portion of the products was characterized either by gas chromatography subsequent to addition of an internal standard (chlorobenzene or carbon tetrachloride) or by ^{1}H NMR employing an internal standard (hexamethyldisiloxane). Products were identified by comparison of gas chromatography retention times and/or spectra with those of authentic samples.

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Registry No. NBS, 128-08-5; *t*-BuOOH, 75-91-2; $(CH_3)_3CCH{=}CH_2$, 558-37-2; $(CH_3)_2CBr(CH_2)_2C(O)NCO$, 82621-92-9; $(CH_3)_2CBr(CH_2)_2C(O)NHC(O)OMe$, 82621-93-0; $CH_3CHBr(CH_2)_2C(O)NCO$, 82621-95-2; $CH_3CHBr(CH_2)_2C(O)NHC(O)OMe$, 82621-96-3; CH_2Cl_2, 75-09-2; $CH_2{=}CCl_2$, 75-35-4; $(CH_3)_2CHCH(CH_3)_2$, 79-29-8; EtPh, 100-41-4; MePh, 108-88-3; 2,2-dimethylglutaric anhydride, 2938-48-9; 2,2-dimethylglutarimide, 1194-33-8; 2-methylglutarimide, 29553-51-3; *N*-bromo-2,2-dimethylglutarimide, 82621-80-5; *N*-bromo-2-methylglutarimide, 82621-79-2; *N*-bromoglutarimide, 3699-18-1; *N*-bromo-3,3-dimethylglutarimide, 66393-63-3; *N*-chloro-3,3-dimethylglutarimide, 82621-83-8; 3,3-dimethylglutarimide, 1123-40-6; oxalyl chloride, 79-37-8; di-*tert*-butyl peroxyoxylate, 1876-22-8; neopentane, 463-82-1; ethene, 74-85-1; butane, 106-97-8; 2-norbornene, 498-66-8; 1,3-butadiene, 106-99-0.

Free Radical Addition of *N*-Bromoglutarimides and *N*-Bromophthalimide to Alkenes. Absolute and Relative Rates

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N-Bromoglutarimides and *N*-bromophthalimide add to electron-rich alkenes, in free radical chain reactions, with yields up to 90%, thus effecting vicinal additions of halogen and amino functions. Relative rates for the addition of *N*-bromo-3,3-dimethylglutarimide (**1a**) and *N*-bromophthalimide (**1b**) to different alkenes show little rate discrimination among electron-rich alkenes, but these imides do not add to electron-deficient alkenes such as maleic anhydride and tetrachloroethylene. A minimum value of the absolute rate constant for the addition step is 10^5 L/mol s at 35 °C. These reactions have good synthesis potential, even with alkenes which would undergo allylic substitution under Ziegler conditions.

The major evidence for the recognition of imidyl radicals as reaction intermediates has depended on substitution reactions with reagents such as *N*-bromosuccinimide (NBS) which replaces H by Br in the substrate.[1] Since the imidyl moiety does not surface as a part of this product, substitution reactions do not provide definitive evidence for the intermediacy of imidyl radicals, such as one obtains from addition reactions.

The small amounts of additions to alkenes of *N*-halo imides, noted by Ziegler and co-workers,[2] have been attributed to the intrusion of ionic processes. Only with tetrafluoro-*N*-bromosuccinimide[3] was this reported to be a major pathway.

We describe here the evidence that the additions are chain reactions inhibited by oxygen, that imidyl radicals are the carriers which add to the alkenes, that imidyls show little discrimination among differently substituted electron-rich alkenes, and that the rate of each step in the addition must be greater than 10^5 M^{-1} s^{-1}. These reactions would be useful in syntheses that would require the additions of amino and halo fragments to alkenes.

The radical chain additions of *N*-bromo imides **1** to alkenes can be photo or peroxide initiated.[3] In these reactions the alkenes serve as both substrate and scavenger of the small amounts of Br· and Br_2 that are produced. Radical chain additions of *N*-bromosuccinimide (NBS) and other *N*-halo imides to alkenes provided unambiguous proof of the intermediacy of imidyl radicals. These high yield reactions largely escaped notice over the preceding four decades because reactions of NBS were mainly restricted to carbon tetrachloride as the solvent,[2] to effect allylic brominations. The low solubility of NBS in carbon tetrachloride ($\sim 10^{-3}$ M) precluded the operation of the imidyl chain.[4] The addition to alkenes is a major reaction channel if the *N*-halo imide is soluble.[1a] Better solubility

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