ether was removed at reduced pressure on a rotary evaporator to obtain 12.7 g of tan oil.

The oil was purified by silica gel chromatography using a Waters Prep 500 HPLC and eluting with 20% ethyl acetate/hexane. Distillation of the major HPLC fractions (the third and fourth 400 mL volumes of eluant) at 0.1 torr afforded 1.75 g (92–100 °C, 97% pure by GLC), 2.04 g (100–102 °C, 99% pure), and 1.08 g (100–103 °C, 97% pure) cuts of purity ≥97% (4.9 g total, 35%). HPLC on a Daicel Chiralpak OP+ column eluted with 0.5% 2-propanol/isooctane indicated a 63:37 *R*/*S* ratio. The optical rotation of the neat 3-phenylcyclohexanone measured in a 10.00-cm cell was α^{26}_D +1.555°.

Acknowledgment. We thank Prof. R. Karl Dieter (Clemson U.) for sharing his results on asymmetric induction via *N*-heterocuprates with us prior to publication. Prof. J. K. Whitesell (U. of Texas—Austin) and Prof. A. I. Meyers and Prof. R. M. Williams (Colorado State) generously provided samples of optically active amines. Prof. M. Diem (Hunter College) kindly measured the CD spectrum of our optically active 3-phenylcyclohexanone.[30]

Imidyl Radicals. The Chemistries of 1,8-Naphthalenedicarboximidyl and Phthalimidyl Radicals

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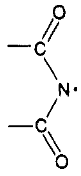
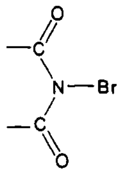
The chemistries of 1,8-naphthalenedicarboximidyl (N•) and phthalimidyl (P•) radicals are described: Hydrogen abstractions from alkanes and additions to olefins and benzene proceed in high yield. The low cost of phthalimide, coupled with the absence of a parasitic ring-opening reaction for P•, makes *N*-bromophthalimide an economical reagent for low-selectivity brominations. The chemistry of N• resembles that of other imidyl radicals (succinimidyl, glutarimidyl) with respect to selectivities. Conversely, P• is somewhat of a maverick among imidyl radicals, being slightly more selective in its reactions, but still 10^2–10^4 less selective than Br•.

Reactions of imidyl radicals (A) remained unrecognized until the importance of two factors became apparent: (1) the necessity to use solvents in which the solubility of the imidyl radical precursor, *N*-halo imide (B), was sufficiently high and (2) the necessity to eliminate competitive chain reactions based on halogen atom (X•), accomplished by including alkenes to selectively scavenge X• and X_2. Consequently, the chemistries of succinimidyl and glutarimidyl radicals became accessible.[1,2]

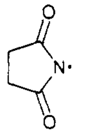


A

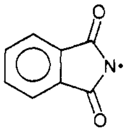


B

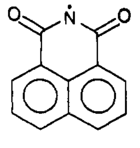
Earlier papers describe the chemistries of succinimidyl[1,2] and, to a lesser extent, phthalimidyl radicals.[2] In this paper, we describe both the chemistry of the 1,8-naphthalenedicarboximidyl radical and additional phthalimidyl chemistry. The behavior of these structurally related radicals is compared. *N*-Bromophthalimide proves to be a low-cost, useful reagent for both Br substitutions and for additions to alkenes and arenes.



succinimidyl (S•)



phthalimidyl (P•)



1,8-naphthalenedicarboximidyl (N•)

Results

In order to observe imidyl chemistry, the following precautions were followed: Reactions were carried out in systems containing alkenes to limit competing bromine atom chain reactions. Dioxygen, an inhibitor of free radical chain reactions, was rigorously excluded. Any HBr which might be produced in these reactions is efficiently scavenged by the *N*-bromo compounds yielding Br_2,[3] which is subsequently removed by addition to the alkene scavenger.

$$\mathrm{HBr} + \mathrm{N{-}Br} \rightarrow \mathrm{NH} + \mathrm{Br_2}$$

A. Reactions of the 1,8-Naphthalenedicarboximidyl Radical (N•). Both 1,8-naphthalenedicarboximide (NH) and N-bromo-1,8-naphthalenedicarboximide (NBr) are readily synthesized from 1,8-naphthalenedicarboxylic acid. A saturated solution of NBr in methylene chloride, a suitable solvent for these reactions, is 0.024 M.

1. Addition of N• to Unsaturated Compounds. As with other *N*-bromo imides,[2,4] the photoinitiated addition of NBr to an alkene produces the corresponding NBr/alkene adduct in good yield (Table I). The observation of the naphthalenedicarboximidyl moiety in the products provides evidence for the presence of N• as the chain carrier. These results are explicable by a chain sequence which involves as a key step, addition of N• to the olefin (Scheme I). Since less than 7% of the initial bromine appears as the *vic*-dibromide of the alkene scavenger, chain lengths greater than 20 are indicated.

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Scheme I

$$\mathrm{Im}^\bullet + \mathrm{C{=}C} \rightarrow \mathrm{Im{-}C{-}C}^\bullet$$

$$\mathrm{Im{-}C{-}C}^\bullet + \mathrm{ImBr} \rightarrow \mathrm{Im{-}C{-}C{-}Br} + \mathrm{Im}^\bullet$$

where Im = imidyl radical ($N^\bullet$, $P^\bullet$, $G^\bullet$, $S^\bullet$)

Analogous evidence for the intermediacy of $N^\bullet$ is obtained from the efficient reaction of NBr with benzene or chlorobenzene (Table I). These reactions show the same stoichiometry and are rationalized by the same mechanism established for other imidyls,[2,5] depicted in Scheme II.

Scheme II

propagation

$$\mathrm{Im}^\bullet + \mathrm{C_6H_6} \rightarrow \mathrm{Im{-}C_6H_6}^\bullet$$

$$\mathrm{Im{-}C_6H_6}^\bullet + \mathrm{ImBr} \rightarrow \mathrm{Im{-}C_6H_6Br} + \mathrm{Im}^\bullet$$

HBr scavenging

$$\mathrm{Im{-}C_6H_6Br} \rightarrow \mathrm{Im{-}C_6H_5} + \mathrm{HBr}$$

$$\mathrm{HBr} + \mathrm{ImBr} \rightarrow \mathrm{ImH} + \mathrm{Br_2}$$

$$\mathrm{Br_2} + \mathrm{CH_2{=}CH_2} \rightarrow \mathrm{BrCH_2CH_2Br}$$

overall

$$2\mathrm{ImBr} + \mathrm{C_6H_6} + \mathrm{CH_2{=}CH_2} \rightarrow \mathrm{Im{-}C_6H_5} + \mathrm{ImH} + \mathrm{BrCH_2CH_2Br}$$

2. Hydrogen Abstraction from Alkanes by $N^\bullet$. The photoinitiated bromination of butane by NBr (in the presence of $CH_2{=}CH_2$ and absence of O_2) occurs readily, forming 1- and 2-bromobutanes in molecular ratio 0.27 (Table II). Under these conditions, $N^\bullet$ is the chain carrier (Scheme III). The selectivity on a per hydrogen basis, r(secondary/primary) = 5.5, is critically distinct from the value of 750 established for $Br^\bullet$,[6,7] the alternate potential chain carrier. The value 5.5 is reminiscent of $Cl^\bullet$ (3.6),[8] $S^\bullet$ (3.5),[1,2,6] and glutarimidyl, $G^\bullet$ (6–7).[2,9]

Scheme III

$$\mathrm{Im}^\bullet + \mathrm{RH} \rightarrow \mathrm{ImH} + \mathrm{R}^\bullet$$

$$\mathrm{R}^\bullet + \mathrm{ImBr} \rightarrow \mathrm{RBr} + \mathrm{Im}^\bullet$$

Similarly, the photoinitiated bromination of 2,3-dimethylbutane (DMB) produces 2- and 1-bromo-2,3-dimethylbutanes in a ratio of 2.6:1 (Table II). The selectivity on a per hydrogen basis, r(tertiary/primary) = 16, contrasts sharply with that of $Br^\bullet$ (150 000)[6,7] and is similar to $S^\bullet$ (14)[1,2,6] and $G^\bullet$ (18).[2,9]

3. Relative Reactivity of $N^\bullet$ toward a Variety of Reagents. Several semiquantitative intermolecular competitions were examined for $N^\bullet$ reactions (Table III). Relative rate constants (molecular base) for reactions of $N^\bullet$ with several substrates were determined: isobutylene (27)/*tert*-butylethylene (21)/ethylene (22)/benzene (16)/neopentane (1.00).

B. Reactions of the Phthalimidyl Radical ($P^\bullet$). 1. Addition of $P^\bullet$ to Unsaturated Compounds. Additions of *N*-bromophthalimide (NBP) to alkenes have been described in some detail.[2,4] These are efficient chain reactions (Scheme I) and provide evidence that the phthalimidyl radical ($P^\bullet$) is the major chain carrier. Additional evidence for intermediacy of $P^\bullet$ is derived from the reaction of NBP with benzene: In the presence of alkene (to scavenge Br_2 formed during the course of the reaction), essentially quantitative yields of *N*-phenylphthalimide are produced, consistent with and therefore calculated by using the stoichiometry depicted in Scheme II.

2. Hydrogen Abstraction from Alkanes by $P^\bullet$. Photoinitiated brominations of alkanes with NBP (solubility 0.2 M in CH_2Cl_2 at 15 °C) in the presence of olefin is an effective procedure, and involves $P^\bullet$ as the major chain carrier (Scheme III). Free of complications and occuring with relatively low selectivities, yields of 80–90% (based upon utilized NBP) can be obtained. The efficiency of the method is indicated by the yield of 1,2-dibromide, which is usually less than 5% the yield of RBr, suggesting a chain length of about 20 (but in some instances as high as 80).

Cyclohexane is converted to cyclohexyl bromide in 86% yield without detectable contamination by dibromide; *trans*-1,2-dibromocyclohexane is a major product when $Br^\bullet$ is the chain carrier.[10]

Butane is converted to a mixture of 1- and 2-bromobutanes. The per hydrogen selectivity, r(secondary/primary), was determined at various temperatures (Table IV). The activation enthalpy and entropy differences (secondary minus primary on a per hydrogen basis) can be calculated: $\Delta\Delta H^* = -0.95$ kcal/mol and $\Delta\Delta S^* = 1.6$ cal/mol·K.

The tertiary/primary intramolecular competition was examined with 2,3-dimethylbutane (DMB). The per hydrogen selectivity, r(tertiary/primary), was found to be 49.

The competitive brominations of neopentane and methylene chloride (Table V) were shown to be insensitive to the amount of *tert*-butylethylene present. The values indicate that the C–H bond of methylene chloride, although the weaker,[11] is nonetheless less reactive (on a per hydrogen basis) toward $P^\bullet$ ($\Delta\Delta H^* = -3.6$ kcal/mol, $\Delta\Delta S^* = -8.6$ cal/mol·K). This deactivation of an electron-deficient C–H bond by chloro substituents is a property found with other imidyls[1,2] and $Cl^\bullet$.[11]

3. Relative Reactivity of $P^\bullet$ toward a Variety of Reagents. In order to describe the selectivity of $P^\bullet$ toward several substrates, several intermolecular competitions were studied. The results are summarized in Table VI. The following reactivity order (molecular base) was determined: isobutylene (200)/*tert*-butylethylene (77)/ethylene (24)/benzene (11)/neopentane (1.00).

Discussion

Table VII summarizes the experimentally observed selectivities of the different imidyls, and several other radicals, toward various substrates. Hydrogen abstractions by imidyl radicals are characterized by a low selectivity for primary, secondary, or tertiary hydrogens, suggesting by analogy to Cl atom,[12] an early transition state for these reactions. However, $Cl^\bullet$ reacts faster in hydrogen abstractions by as great as four to five powers of ten.[2,4,13,14,15] Imidyl radicals are electrophilic in nature; additions occur only to electron-rich olefins.[2,4] Further, the rate of addition of imidyl to ethylene relative to benzene ($P^\bullet$, 2.7; $N^\bullet$, 1.3; $G^\bullet$, 4.0) resembles that of hydroxyl ($HO^\bullet$, 0.23), whereas

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Table I. Reactions of *N*-Bromo-1,8-naphthalenedicarboximide (NBr) with Unsaturated Compounds

	reactants, mmol[a]			
T, °C	NBr	unsatd compd	major product (%)[b,c]	other products (%)[b]
17	1.04	$(CH_3)_2C{=}CH_2$, 19.1	$(CH_3)_2C(Br)CH_2$-N (82)	$BrCH_2C(CH_3)C{=}CH_2$ (6.5) $(CH_3)_2C(Br)CH_2Br$ (6.8)
17	1.97	$(CH_3)_3CCH{=}CH_2$, 20.9	$(CH_3)_3CCHBrCH_2$-N (68)	$(CH_3)_3CCHBrCH_2Br$ (4.1)
70	1.23	C_6H_6, 56.3[d]	Ph-N (79[e])	$BrCH_2CH_2Br$ (89[e])
70	0.83	C_6H_5Cl, 49.1[d]	ClC_6H_4-N (100[e])	$BrCH_2CH_2Br$ (95[e])

[a] 10 mL (156 mmol) of CH_2Cl_2 as solvent. Reactions photoinitiated with 400-W medium-pressure mercury arc lamp through two layers of Pyrex for at a distance of ca. 10 cm for 1–6 h. [b] Based upon reacted NBr. [c] N = *N*-1,8-naphthalenedicarboximidyl. [d] 2 mmol of $CH_2{=}CH_2$ present to scavenge $Br_2/Br^\bullet$. [e] Based on $2NBr + C_6H_5X + CH_2{=}CH_2 \rightarrow N\text{-}C_6H_4X + NH + BrCH_2CH_2Br$.

Table II. Reactions of *N*-Bromo-1,8-naphthalenedicarboximide (NBr) with Alkanes

reactants, mmol[a]			
NBr	alkane	products (%)[b]	selectivity[c]
1.01	butane, 19.6	2-bromobutane (54.9); 1-bromobutane (15.0); $CHBrCl_2$ (3.4); $BrCH_2CH_2Br$ (23.4)	*r*(secondary/primary)[d] = 5.48
1.03	2,3-dimethylbutane, 15.4	2-bromo-2,3-dimethylbutane (36.8); 1-bromo-2,3-dimethylbutane (14.0); $CHBrCl_2$ (2.8); $BrCH_2CH_2Br$, 14.2	*r*(tertiary/primary)[e] = 15.8

[a] 10 mL (156 mmol) of CH_2Cl_2 solvent, ethylene (1.4–1.5 mmol) present to scavenge $Br_2/Br^\bullet$, photoinitiated with 400-W medium-pressure mercury arc lamp through two layers of Pyrex for 0.5–3 h. [b] Based upon reacted NBr. [c] *T* = 17 °C. [d] *r*(secondary/primary) = (yield secondary RBr/yield primary RBr)(6/4). [e] *r*(tertiary/primary) = (yield tertiary RBr/yield primary RBr)(12/2).

Table III. Competitive Reactions of 1,8-Naphthalenedicarboximidyl Radical ($N^\bullet$)

		reactants, mmol				
T, °C	*t*, h	NBr[a]	A	B	products (%)[b]	k_A/k_B[c]
17	6	2.01[d]	butane, 19.7	$CH_2{=}CH_2$,[g] 11.5	2-bromobutane (21.1) 1-bromobutane (5.83) $CHBrCl_2$ (0.7) $BrCH_2CH_2$-N (36.5) $BrCH_2CH_2Br$ (21.4)	0.43
17	6	1.97[d]	neopentane, 20.8	*t*-$BuCH{=}CH_2$, 22.4	neopentyl bromide (2.74) N-$CH_2CH(Br)C(CH_3)_3$[e] (61.0) $(CH_3)_3CCHBrCH_2Br$ (3.9)	0.048
17	1	1.92[d]	neopentane, 11.0	isobutylene, 11.7	$(CH_3)_3CCH_2Br$ (1.51) N-$CH_2CBr(CH_3)_2$[e] (44.0) $(CH_3)_2CBrCH_2Br$ (11.4) $BrCH_2C(CH_3){=}CH_2$ (4.0)	0.037
70	3	1.42	C_6H_6, 22.5	isobutylene, 19.8	N-C_6H_5[e] (36.8[f]) N-$CH_2CBr(CH_3)_2$[e] (27.4) $(CH_3)_2CBrCH_2Br$ (38.6[f]) $BrCH_2C(CH_3){=}CH_2$ (22.9)	0.59
70	3	0.76	C_6H_6, 22.5	$CH_2{=}CH_2$, 7.82	N-C_6H_5[e] (72.3[f]) N-CH_2CH_2Br[e] (22.5) $BrCH_2CH_2Br$ (71.6[f])	0.49

[a] *N*-Bromo-1,8-naphthalenedicarboximide, photoinitiated with a 400-W medium-pressure mercury arc lamp at a distance of ca. 10 cm through two layers of Pyrex. [b] Based upon reacted NBr. [c] Relative rate constants for reaction with $N^\bullet$ (molecular basis). [d] 10 mL (156 mmol) of CH_2Cl_2 solvent. [e] N = *N*-1,8-naphthalenedicarboximidyl. [f] Based upon $2NBr + C_6H_5X + \text{olefin} \rightarrow N\text{-}C_6H_4X + NH + \text{dibromide}$. [g] Amounts of C_2H_4 in solution. See ref 5, Table V, footnote *g*.

Table IV. Reactions of *N*-Bromophthalimide (NBP) with Butane in CH_2Cl_2

	reactants, mmol[a]			products, mmol				
T, °C	NBP	butane	olefin	2-bromobutane	1-bromobutane	$CHBrCl_2$	dibromide[b]	*r*(secondary/primary)[c]
13[d]	1.31	20.5	1.44[e]	0.479	0.061		0.027	11.8
35[f]	3.53	2.4	0.389[g]	0.0958	0.00886	0.0618		10.1
70[d]	1.23	20.2	1.76[e]	0.420	0.071	0.018	0.015	8.9

[a] 5 mL (78 mmol) of CH_2Cl_2 solvent. [b] $BrCH_2CH_2Br$ from $CH_2{=}CH_2$, *t*-$BuCHBrCH_2Br$ from *tert*-butylethylene. [c] *r*(secondary/primary) = (yield secondary RBr/yield primary RBr)(6/4). [d] Photoinitiated with a 400-W medium-pressure mercury arc lamp at a distance of ca. 10 cm through two layers of Pyrex for 3–6 h. [e] $CH_2{=}CH_2$. [f] Thermally initiated with 1 mol % di-*tert*-butyl peroxyoxalate (TBPO), maintained at 35 °C for 1.25 h. [g] *tert*-Butylethylene.

for a nucleophilic radical (e.g., methyl), addition to ethylene is favored by a factor of 100.[2]

ESR spectroscopy indicates a π-ground state for succinimidyl radical ($S^\bullet$), with approximately 60% spin density at nitrogen.[16] This assignment of a π-ground state receives additional support from ab initio calculations.[17] Therefore, the most reasonable supposition is that the observed chemistry of succinimidyl is attributable to the π-ground state.[18] Undoubtedly, the electrophilic character

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Table V. Reaction of *N*-Bromophthalimide (NBP) with Neopentane in CH_2Cl_2

	reactants, mmol			products, mmol		
T, °C	NBP[a]	*tert*-butylethylene	neopentane	$(CH_3)_3CCH_2Br$	$CHBrCl_2$	$r(Me_4C/CH_2Cl_2)$[b]
10[c]	0.913	0.389	3.83	0.055	0.025	7.4
10[c]	2.78	0.311	3.98	0.039	0.017	7.4
10[c]	2.87	0.466	3.92	0.050	0.022	7.4
10[c]	3.17	0.117	4.05	0.022	0.010	7.4
36[d]	2.86	0.47	4.06	0.015	0.011	4.3
36[d]	3.27	0.23	4.19	0.016	0.011	4.5
36[d]	3.27	0.31	3.96	0.012	0.009	4.4

[a] 5.0 mL (78 mmol) of CH_2Cl_2 solvent. [b] $r(Me_4C/CH_2Cl_2)$ = (yield neopentyl bromide/yield $CHBrCl_2$)(2/12)($[CH_2Cl_2]/[Me_4C]$). [c] Photoinitiated with a 400-W medium-pressure mercury arc lamp at a distance of ca. 10 cm through two layers of Pyrex for 4–19 h. [d] Photoinitiated with a 275-W sun lamp through two layers of Pyrex for 2 h.

Table VI. Competitive Reactions of the Phthalimidyl Radical (R•)

	reactants, mmol[a]				
T, °C	NBP[b]	A	B	products, mmol[c]	k_A/k_B[d]
11	1.11	Me_4C, 8.71	*tert*-butylethylene, 1.94	neopentyl bromide, 0.030 $P{-}CH_2CHBrC(CH_3)_3$,[e] 0.703	0.012
19	0.94	Me_4C, 6.74	*tert*-butylethylene, 1.94	neopentyl bromide, 0.030 $P{-}CH_2CHBrC(CH_3)_3$,[e] 0.641	0.014
70	0.68	C_6H_6, 56.3	$CH_2{=}CH_2$, 10.1	$P{-}C_6H_5$,[e] 0.276 $P{-}CH_2CH_2Br$,[e] 0.110 $BrCH_2CH_2Br$, 0.290	0.45
70	0.96	C_6H_6, 56.3	*tert*-butylethylene, 19.5	$P{-}C_6H_5$,[e] 0.127 $P{-}CH_2CHBrC(CH_3)_3$,[e] 0.320 $BrCH_2CHBrC(CH_3)_3$, 0.170	0.14

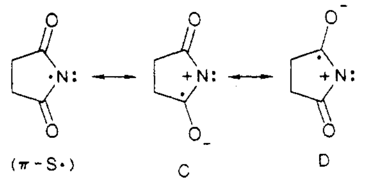
[a] 4–5 mL of CH_2Cl_2 solvent, photoinitiated with a 400-W medium-pressure mercury arc lamp at a distance of ca. 10 cm through two layers of Pyrex for 0.5–3 h. [b] *N*-Bromophthalimide. [c] Listed products and unreacted NBP account for >.0% of initial NBP. [d] Relative rate constants (molecular base) for reaction with P•. [e] P = *N*-phthalimidyl. [f] Amounts of C_2H_4 in solution. See ref 5, Table V, footnote *g*.

Table VII. Selectivities of Imidyl (and Other) Radicals toward Various Reagents

reagent	succinimidyl (S•)[a]	glutarimidyl (G•)[b,c]	phthalimidyl (P•)[b,d]	naphthimidyl (N•)[d]	chlorine atom[e]	phenyl (Ph•)
tertiary H	14	18	49	16	4.2	40
secondary H	4.6	6.6	12	5.5	3.6	8.4
primary H	1.00	1.00	1.00	1.00	1.00	1.00
CH_2Cl_2	0.06	0.1	0.1		<0.02	0.05
$CH_2{=}CH_2$		280	380	260		
$t\text{-}BuCH{=}CH_2$	80	100	1000	250	58	171
$(CH_3)_2C{=}CH_2$		140	2600	330		445
vinyl acetate		224	1222			
$CH_2{=}C(Cl)CH_3$		204	980			
C_6H_6		70	140	200		

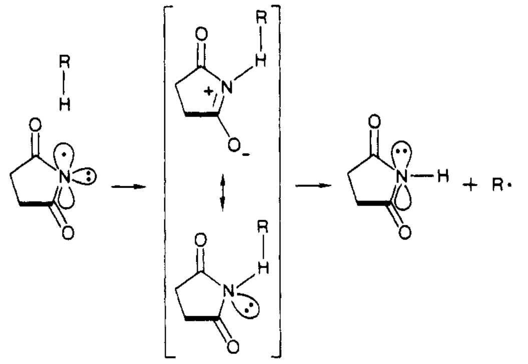
[a] Reference 6. [b] Reference 4. [c] Reference 9. [d] This work. [e] Reference 8. [f] Reference 24.

of this radical can be rationalized as a consequence of (a) contributions of canonical structures C and D to the resonance hybrid description of S• and/or (b) the electronegativity of nitrogen. The low rate of imidyl radical reactions (relative to Cl•) might be attributed to the presence of less than 100% spin density at nitrogen, due to interaction of the unpaired electron with the carbonyls.


(π-S•) C D

Delocalization of the *nonbonding* electron pair on nitrogen should stabilize the *transition state* of imidyl reactions, perhaps explaining the low selectivity associated with imidyl radicals (Scheme IV).

Scheme IV



Contributions from these competing (and contradictory) ground- and transition-state interactions involving the π-system (carbonyls) are undoubtedly responsible for the anomolous behavior of imidyls and for the apparent breakdown of the reactivity-selectivity principle (RSP) in their reactions.

Extension of the π-system has little effect on the selectivity of imidyl radicals: S•, G•, and N• exhibit nearly identical selectivity; P• is slightly more selective (Table

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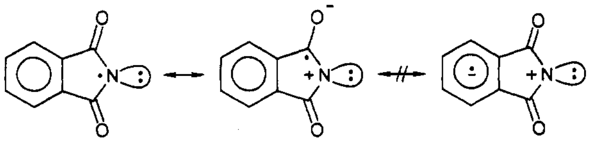
(18) Conversely, stereoelectronic considerations for the production of imidyl radicals or for the ring-opening reaction, indicate that the observed chemistry may be best attributed to the σ-state; the chemistry of the π-ground-state radical may be unknown.[19]

(19) Skell, P. S.; Lüning, U.; McBain, D. S.; Tanko, J. M. *J. Am. Chem. Soc.* 1986, *108*, 21.

VII). These observations suggest that minimal spin density is delocalized into the aromatic ring[18] (eq 1).


(1)

Conclusion

This paper has examined the effect of structure variation on the reactivity of imidyl radicals. The selectivities of most imidyl radicals (succinimidyl, glutarimidyl, naphthalenedicarboximidyl) parallel those of chlorine atom, whereas the phthalimidyl radical tends more to be slightly more selective, resembling phenyl or *tert*-butoxy radicals. Assuming a π-structure for imidyl radicals, the effect of the π-system (carbonyls) on reactivity is poorly understood. The relationship between the structure and reactivity of imidyl radicals remains a topic of experimental and theoretical interest.

Experimental Section

^{1}H NMR spectra were recorded on either a Varian EM-360 (60 MHz) or Bruker WH-200 (200 MHz) spectrometer, with chemical shifts reported on the δ scale relative to hexamethyldisiloxane ($\delta = 0.07$). Mass spectra were taken on a Kratos 9/50 at 70 eV. Gas chromatographic analyses were carried out on either a Hewlett-Packard HP 5790 A FID or HP 5890, each equipped with a DB-5 capillary column (30 m × 0.25 mm) and a HP 3390 A integrator.

Materials. Dichloromethane was distilled from phosphorus pentoxide, the middle cut was taken, and the purity was checked by GLC (>99.99%). Benzene (Fisher) was purified by two recrystallization cycles and was dried with molecular sieves (>99.98%). Di-*tert*-butyl peroxyoxalate (TBPO) was prepared as described.[20] The following were used without further purification: *n*-butane (Matheson), ethene (Matheson, research grade, >99.99%), isobutene (Matheson), tetrachloromethane (Fisher), bromine, chlorobenzene, 1,2-dibromoethene, 2,3-dimethylbutane, 3,3-dimethylbutene, hexamethyldisiloxane, 1,8-naphthalenedicarboximide, and potassium phthalimide (all Aldrich).

***N*-Bromophthalimide (NBP).** Bromine (2.5 mL, 48.7 mmol) was added dropwise to a vigorously stirred slurry containing potassium phthalimide (8.0 g, 43.2 mmol) and sodium bicarbonate (3.7 g, 43.2 mmol) in 200 mL of water at 0 °C. After the bromine color was sufficiently discharged, the solid was isolated by suction filtration and washed with cold water. The solid was extracted with small amounts of cold methanol, air-dried, and then pumped to dryness under high vacuum: yield, 6.5 g (65%); mp 198–202 °C (lit. mp 206 °C).[21] The material was assayed by iodometric titration (>97% purity) and used without further purification.

***N*-(2-Bromoalkyl)phthalimides.** The preparation of the NBP/alkene addition products has been previously described.[4]

***N*-Phenylphthalimide.** NBP and benzene were degassed in a 30-mL Pyrex pressure tube (equipped with an O-ringed Teflon needle valve) via the freeze–pump–thaw method (3x). The heterogeneous solution was placed in a water bath and irradiated (with stirring) by using a 400-W medium-pressure mercury arc lamp from a distance of 5 cm through two Pyrex layers for 3 h. Evaporation of the volatile materials by a trap-to-trap distillation led to crude *N*-phenylphthalimide, which was recrystallized from CCl_4/pentane. $C_{14}H_9NO_2$ (223.29): mp 201–203 °C (lit. mp 204–205 °C);[22] ^{1}H NMR (60 MHz) 7.4 (br s, 5 H), 7.75 (br s, 4 H); MS, *m/z* (relative intensity) 223 (100, M^+), 179 (72), 104 (26), 76 (69).

***N*-Bromo-1,8-naphthalenedicarboximide (NBr).** 1,8-Naphthalimide (6.0 g, 30 mmol) was dissolved in a solution containing KOH (5.0 g, 89 mmol) in 100 mL of water. This solution was cooled to 0 °C, stirred vigorously, while Br_2 (3.0 mL, 59 mmol) in 50 mL CH_2Cl_2 was added dropwise. After the addition of bromine was complete, the resulting yellow precipitate was removed by suction filtration, washed successively with dilute KOH (aqueous) and water, and dried (in vacuo) for 3 h: yield, 5 g (60%); mp 245–249 °C; ^{1}H NMR (60 MHz) 7.5–8.8 (m, 6 H); MS, *m/z* (relative intensity) 277, 275 (4, 4, M^+), 197 (100, M – Br), 153 (37), 126 (32). The material was assayed by iodometric titration (>97% purity) and used without further purification.

General Procedure for the Synthesis of the *N*-(2-Bromoalkyl)-1,8-naphthalenedicarboximides (NBr/Alkene Adducts) and *N*-Phenyl-1,8-naphthalenedicarboximide. NBN, CH_2Cl_2 (solvent), and alkene (or NBN and benzene) were degassed in a 30-mL pressure tube 3x by the freeze–pump–thaw procedure. The solutions were placed in a thermostatically maintained water bath and irradiated with a 400-W medium-pressure mercury arc lamp at a distance of 5 cm through two Pyrex layers for 1–3 h. Trap-to-trap distillation removed the volatiles and led to the crude products, which were purified by dissolution in CCl_4 or hexane and recrystallization after addition of pentane.

***N*-(2-Bromoethyl)-1,8-naphthalenedicarboximide**: $C_{14}H_{10}NO_2Br$ (304.21); mp 173–174 °C; ^{1}H NMR (60 MHz) 7.5–8.7 (m, 6 H), 4.5 (t, $J = 7$ Hz, 3.6 (t, $J = 7$ Hz); MS, *m/z* (relative intensity) 305, 303 (32, 32, M^+), 224 (52, M – Br), 210 (42, M – CH_2Br), 197 (100, M – C_2H_4Br).

***N*-(2-Bromo-2-methylpropyl)-1,8-naphthalenedicarboximide**: $C_{16}H_{14}NO_2Br$ (332.26); mp 108–109 °C; ^{1}H NMR (60 MHz) 7.5–8.7 (m, 6 H), 4.65 (s, 2 H), 1.8 (s, 6 H); MS, *m/z* (relative intensity) 252 (100, M – Br), 236 (97), 210 (64, M – C_3H_6Br), 198 (23, M – C_4H_8Br).

***N*-(2-Bromo-3,3-dimethylbutyl)-1,8-naphthalenedicarboximide**: $C_{18}H_{18}NO_2Br$ (360.32); mp 126–127 °C; ^{1}H NMR (60 MHz) 7.5–8.7 (m, 6 H), 4.0–5.2 (m, 3 H), 1.2 (s, 9 H); MS, *m/z* (relative intensity) 359, 361 (31, 31, M^+), 280 (15, M – Br), 224 (13, M – C_4H_9Br), 210 (52, M – $C_5H_{10}Br$), 197 (100, M – $C_6H_{12}Br$).

***N*-Phenyl-1,8-naphthalenedicarboximide**: $C_{18}H_{11}NO_2$ (273.35); mp 185–190 °C (lit. mp 202 °C);[23] ^{1}H NMR (60 MHz) 7.5–8.7 (m, 6 H), 7.4 (s, 5 H); MS, *m/z* (relative intensity) 273 (99, M^+), 272 (100), 228 (34), 180 (39), 126 (30).

Competition Experiments: General Procedure. *N*-Bromo imide, solvent(s), and other added reagents in a 30-mL Pyrex pressure tube (sealed with an O-ringed Teflon needle valve) were degassed by using the freeze–pump–thaw technique (3–5x). The mixtures were irradiated (thru Pyrex) with a 400-W medium-pressure mercury arc lamp in a thermostatically maintained water bath. Volatiles and nonvolatiles were separated by trap-to-trap vacuum distillation. The volatiles (Me_3CCH_2Br, $CHBrCl_2$, C_4H_9Br's, $C_6H_{13}Br$'s, etc.) were analyzed by GLC (against an appropriate internal standard, usually PhCl). Retention times of products were compared to that of an authentic sample. The nonvolatiles (ImH, ImBr/alkene adduct, *N*-phenyl imides, etc.) were analyzed by ^{1}H NMR (60 or 200 MHz, depending on the complexity of the signal) vs. hexamethyldisiloxane as an internal standard. Unreacted NBP or NBr were quantitated iodometrically with an aliquot of the nonvolatiles.

Reaction conditions and yields are listed in the tables.

Acknowledgment. Financial support for this work came from the National Science Foundation.

Registry No. NBP, 2439-85-2; NH, 81-83-4; NBr, 105089-47-2; DMB, 79-29-8; N$^\cdot$, 105089-50-7; P$^\cdot$, 66393-65-5; C_6H_6, 71-43-2; $(CH_3)_2C{=}CH_2$, 115-11-7; $(CH_3)_3CCH{=}CH_2$, 558-37-2; C_6H_5Cl, 108-90-7; Me_4C, 463-82-1; Me_3CCH_2Br, 630-17-1; potassium phthalimide, 1074-82-4; *N*-phenylphthalimide, 520-03-6; *N*-(2-bromoethyl)-1,8-naphthalenedicarboximide, 74731-94-5; *N*-(2-bromo-2-methylpropyl)-1,8-naphthalenedicarboximide, 105089-48-3; *N*-(2-bromo-3,3-dimethylbutyl)-1,8-naphthalenedicarboximide, 105089-49-4; *N*-phenyl-1,8-naphthalenedicarboximide, 6914-98-3; *N*-(chlorophenyl)-1,8-naphthalenedicarboximide, 105089-51-8; butane, 106-97-8; 2-bromobutane, 78-76-2; 2-bromo-2,3-dimethylbutane, 594-52-5.

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