prepared, using this technique, a number of different functionalized fluorocarbon polymers with varying physical, thermal, and chemical properties which should compliment or compete in applications established for the sulfonic acid functionalized fluorocarbon polymer "Nafion" which has been previously reported.⁸

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Addition Reactions of Imidyl Radicals with Olefins and Arenes

Sir:

Hydrogen abstracting reactions of succinimidyl radical have been described.^{1,2} We report here the facile radical-chain additions of NBS to both alkenes and arenes, and also selectivities different from those known from carbon radical chemistry.

The addition reactions are carried out using a 3:1 mol ratio of olefin/N-haloimide in methylene chloride, chloroform, or carbon tetrachloride as solvents. These reactions may be photoinitiated through Pyrex using a medium-pressure mercury arc lamp as a light source, or thermally initiated with benzoyl peroxide at reflux temperatures; both methods are effective, yields being 40-80%. In the absence of initiation no reaction occurs.³

The products (shown below) of alkene-haloimidyl radical-chain reactions have been isolated as pure solids, and structures proven with ¹H NMR spectroscopy. Chromatography over alumina was employed in the purifications, attended by hydrolysis to the corresponding alcohol in the case of the styrene adduct only.



The failure of dark reactions and the absence of rearrangement products in the reactions of *tert*-butylethylene rule



Scheme II



out an ionic reaction mechanism. The presence of the imidyl moiety on the terminal atom of *tert*-butylethylene and styrene adducts make clear the chain sequence shown in Scheme I.

In methylene chloride solvent olefins with allylic hydrogens react similarly, the additions and the allylic substitutions being closely competitive processes. For example cyclohexene and N-chlorosuccinimide react to give $\sim 50\%$ adduct and $\sim 50\%$ substitution products 3- and 4-chlorocyclohexene.

The same reaction conditions as above are effective for substitution in arene systems,⁴ for example, reactions carried out with benzene and *tert*-butylethylene in 6:1 ratio results in 1:1:1 mol ratio N-phenylated imide, imide, and dibromo adduct of *tert*-butylethylene (Scheme II); in these circumstances there is no loss of NBS to ring-opening product β -bromopropionyl isocyanate. Also, small amounts (~10%) of the *tert*-butylethylene-NBS adduct are obtained. The yield of N-phenylsuccinimide is 45% based on NBS consumed; the theoretical yield is 50%.

Employing the same reactant ratios, similar results are obtained with substituted aromatics, for example, tert-butylbenzene, chlorobenzene (45% o-, 28% m-, 28% p- with Nbromo-3,3-dimethylglutarimide (NBDMG)), p-dichlorobenzene, and napthalene (66% α -, 33% β - with NBS). With anthracene ring-brominated products occur along with imidation products. Aromatic substrates possessing benzylic hydrogens, such as toluene and p-xylene, yield substantial amounts of benzylic bromide product. For example, toluene and NBDMG at 65 °C yield a product mixture consisting of 65% benzyl bromide and 35% imidation product (48% o-, 31% m-, and 21% p-). In these cases, however, use of lower reaction temperatures (0 °C or lower) shifts the product composition in favor of ring imidation. The reaction of toluene with NBDMG at -20 °C gave a mixture, of which more than 80% was imidation product.

In accord with considerations discussed elsewhere,⁵ the chemistry described here is attributed to excited-state imidyl radicals, S_2 , which have been identified with the σ_0 or σ_N states.⁶ The intermediacy of a σ_N imidyl radical seems most likely in view of the addition product structures, with the nitrogen atom of the imidyl moiety bonded to one of the carbons of the olefin or arene.

The relative reactivities of these S_2 species has been probed with two types of competition systems, C-H abstraction vs. alkene addition and alkene addition vs. arene addition.

In the competition between neopentane and addition to *tert*-butylethylene (TBE), with succinimidyl radical, $(k_{(CH_3)_4C}/k_{TBE}) = 0.15$, or 0.04 when calculated on a per methyl group basis. The value of Cl- choosing between abstraction at the methyl position of 1-butene and addition to the double bond, $(k_{abstr}/k_{addn}) = 0.053.^7$ The concordance of

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values emphasises the similarity of Cl- and succinimidyl $(S_2 \cdot).$

Addition competitions between benzene and tert-butylethylene with succinimidyl radical lead to the value $(k_{C_{6}H_{6}}/k_{TBE}) = 2.0$. Although values of 0.01-0.02 are reported for CH_3 and CF_3 ,⁸ there is precedent in OH chemistry for relative rates of 1-4 for additions to substrates of this kind, reactions which occur with absolute rates of 10⁸-10⁹ L mol⁻¹ s⁻¹, encounter-controlled processes.⁹ Thus it seems reasonable to ascribe a similar absolute reaction rate to the S2. succinimidyl radical additions to these substrates.

The substrate styrene is an especially interesting one since it has both alkene and arene moieties in the same molecule, and the vinyl group is generally considered to be unusually reactive for additions of radicals. Addition of 3,3-dimethylglutarimidyl radical occurs on the alkene 2.0 times as fast as to the arene portion of the molecule.

These results indicate that reactions of S_2 , Cl-, and $\cdot OH$ are similar and are relatively insensitive to structural features of the substrate. The transition states may be described in terms of a slightly perturbed substrate molecule with a nearby imidyl radical; by contrast, carbon radicals have stronger bonds to the substrates in both addition and abstraction reactions.^{8a}

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Excited-State Succinimidyl Radical in Thermal Chain Reactions

Sir:

The chemical properties of succinimidyl radicals remained a mystery until the simultaneous recognition in the laboratories of Professor J. G. Traynham¹ and ours² that the radical could be a chain carrier in the sense first suggested by Bloomfield,³ albeit incorrectly⁴ for the allylic bromination reaction.

For substrates which react readily with bromine atoms, succinimidyl mediated brominations are carried out in the presence of bromine scavengers (ethylene or tert-butylethylene), employing a good solvent for NBS such as methylene chloride. In these circumstances bromination occurs with a selectivity which closely resembles Cl. mediated chlorinations.

Table I

 $neo C_5 H_{12}$ XH + $neo C_5 H_{11}$.

CH_2Cl_2	⁻ XH	+	$\cdot \text{CHCl}_2^{\mathfrak{a}}$
			00-2

Reagent ^b (no. of experiments; % yields)	$(k_{neo-C_5H_{12}}/k_{CH_2Cl_2})/H_{1}$
NBS-olefin (2; 4)	21.3 ± 2.0
NBS-Br ₂ (6; 14-96)	1.15 ± 0.16
NIS-I ₂ $(4; 1-6)^{c}$	1.15 ± 0.12
NBP-olefin (2; 6-12)	12.1 ± 0.4
NBP-Br ₂ $(5; 1-20)$	0.51 ± 0.13
$NIP-I_2(2; 5-11)$	0.50 ± 0.02
NBDMG-olefin (2; 52)	3.9 ± 0.2
NBDMG-Br ₂ (1; 38)	1.0
Br_2^d (1; 3)	0.1
Cl ₂ (2; 95)	>100

^a In all experiments ne_0 -C₅H₁₁· is trapped to yield only neopentyl halide, while CHCl₂, in addition to being trapped with halogenating agent to yield CHXCl₂, also adds to ethylene to yield, ultimately, 1,1-dichloro-3-halopropane. With low olefin and N-bromoimide concentration 1,1,2,2-tetrachloroethane from coupling of the dichloromethyl radical is observed. Relative rates in N-haloimide-olefin experiments were calculated using yields of neopentyl halide, halodichloromethane, halodichloropropane, and tetrachloroethane. b NXS = N-halosuccinimides; NXP = N-halophthalimides; NBDMG = N-bromo-3,3-dimethylglutarimide. ^c The NIS-allene system, in which I2 is virtually eliminated, yields results similar to the NBSolefin system. Although reliable quantitative results are not available in this case, unambiguously, the products from ·CHCl₂ were minor compared to neopentyl iodide. d Bromination is slow, 3% consumption of bromine after 4-h irradiation.

$$\frac{Br}{1} + succinimide^2$$

Glutarimidyl, 3,3-dimethylglutarimidyl, phthalimidyl, and several hydantoyl radicals also show hydrogen-abstracting properties.

We make here a preliminary report that our results require the presence of two radicals in these systems, a ground state (S_1) and an excited state radical (S_2) . This conclusion may have significance similar to that generated by the earlier suggestion that two carbene states were required to rationalize carbene chemistry.

Imidyl radicals can be generated as reaction intermediates in (1) the presence of bromine scavenger olefins, as indicated above, or (2) by the use of the N-haloimide and free halogen when using substrates which do not react readily with the bromine atom (neopentane, tert-butyl chloride, CH₂Cl₂, as examples).⁵ The imidyl radicals generated by these two procedures show strikingly different reactivities. Results for competitive halogenations of neopentane and methylene chloride are shown in Table I.

In all competitions, mole ratios of substrate (neopentane, $CH_2Cl_2)/N$ -haloimide were 30 or more. The competitions with N-haloimide-olefin reagent were carried out using methylene chloride/neopentane mixtures (mole ratios between 8 and 300), methylene chloride functioning as both substrate and solvent; an N-haloimide/olefin ratio of 2.0 was generally used in order to keep addition product formation to a minimum. In competition experiments using N-haloimide- X_2 reagent, molar ratios of methylene chloride/neopentane between 2 and 16 were employed and N-haloimide/ X_2 ratios of 0.5 to 100. All competiton reactions were photoinitiated after degassing and were conducted at 15 °C. Bromoimide-Br2 systems are efficiently initiated at wavelengths >400 nm; the bromoimideolefin systems are initiated only with wavelengths between 280 and 350 nm. In bromination reactions irradiation times of