

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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References and Notes

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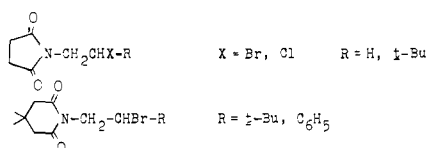
Addition Reactions of Imidyl Radicals with Olefins and Arenes

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.

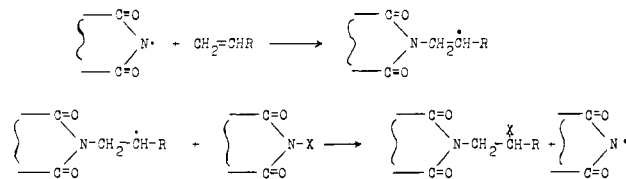
The addition reactions are carried out using a 3:1 mol ratio of olefin/*N*-haloimide in methylene chloride, chloroform, or carbon tetrachloride as solvents. These reactions may be photoinitiated through Pyrex using a medium-pressure mercury arc lamp as a light source, or thermally initiated with benzoyl 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.

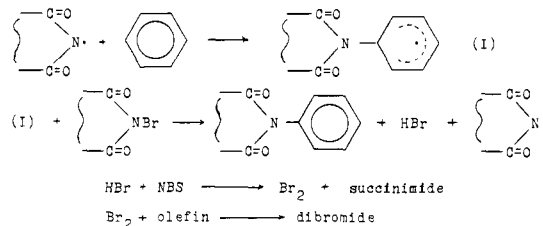


The failure of dark reactions and the absence of rearrangement products in the reactions of *tert*-butylethylene rule

Scheme I



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 ~50% adduct and ~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 *N*-bromo-3,3-dimethylglutarimide (NBDMG)), *p*-dichlorobenzene, and naphthalene (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% benzylic 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_{O} 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, ($k_{(\text{CH}_3)_4\text{C}}/k_{\text{TBE}}$) = 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, ($k_{\text{abstr}}/k_{\text{addn}}$) = 0.053.⁷ The concordance of

