J. Org. Chem. **1997,** *62,* 5959−5965

Regiochemistry of Diels−Alder Reactions of Diverse *β*-Functionalized Alkynyliodonium Salts with Unsymmetrical Dienes

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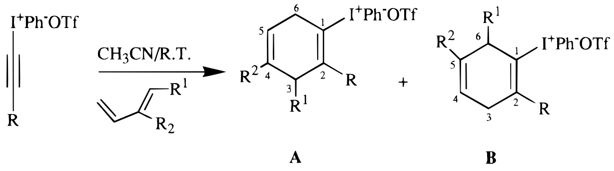
Received April 11, 1997[⊗]

The reaction of alkynyliodonium salts with unsymmetrically substituted dienes at room temperature in acetonitrile results in iodonium-substituted cyclohexadienes via Diels−Alder cycloaddition. A number of dienes were tested, and the regioselectivity of the reaction was investigated. The X-ray crystal structure for 1-(trimethylacetyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-methyl-1,4-cyclohexadiene (**3**) is reported.

Introduction

The Diels−Alder reaction is arguably the best known and extensively used named reaction. It has been the center of numerous synthetic, theoretical, and mechanistic studies and has been extensively reviewed since its discovery in 1928 by Otto Diels and Kurt Alder.[1] Investigations of the Diels−Alder reaction have led to the incorporation of a great deal of variability in the substrates, including heteroatoms and a wide variety of functionality.[2−5] A high degree of regiochemical selectivity and predictability occurs as well. The wide variability and predictability have led to the extensive use of the Diels−Alder reaction in synthesis. Of the substrates that may be used are unfunctionalized carbon−carbon double and triple bonds, but they are usually unreactive as dienophiles and require elevated temperatures and pressures in order to participate.[6] Electron-withdrawing functionality on a dienophile can dramatically activate it as a participant in the Diels−Alder reaction. Acetylene is known to undergo Diels−Alder cycloaddition reactions when it has electron-withdrawing groups at one and/or both ends of the carbon−carbon triple bond or through the use of elevated temperatures and/or pressures. It is desirable to identify a group that activates acetylenes to the Diels−Alder reaction using mild reaction conditions while allowing the incorporation of a variety of functionality. This goal has been reached via the Diels−Alder cycloaddition reaction of alkynyliodonium salts.[7]

Recently we reported a method for the formation of a wide variety of *β*-functionalized alkynyl(phenyl)iodonium salts and demonstrated their ability to undergo Diels−Alder cycloaddition reactions with symmetrical dienes such as cyclopentadiene and 2,3-dimethylbutadiene under very mild reaction conditions.[7] In addition, the resulting cycloadducts contain a vinyl(phenyl)iodonium moiety, and such species are known to be excellent vinyl cation synthons which react with a wide range of nucleophiles such as organocopper reagents, enolates, and *p*-toluenesulfinate.[8] It is the highly electron withdrawing nature of the iodonium moiety that activates the carbon−carbon triple bond and allows it to react as a Diels−Alder substrate. It was also thought that because this electron-withdrawing nature polarizes the triple bond, it would have excellent potential for undergoing regiospecific Diels−Alder reactions. It has been well demonstrated in the literature that the reaction of unsymmetrical substrates in the Diels−Alder reaction can result in regioselectivity. Hence, it was of interest to examine the regioselectivity of a variety of *β*-substituted alkynyl(phenyl)iodonium salts with unsymmetrical dienes. The Diels−Alder cycloaddition reaction of alkynyl(phenyl)iodonium salts with unsymmetrically substituted dienes can result in the formation of two different products (**A** and **B**, eq 1). In this paper we report the reaction of a number of *β*-functionalized alkynyl(phenyl)iodonium salts with several unsymmetrical dienes which lead to substituted cyclohexadiene iodonium species and in some cases exhibit excellent regioselectivity.



A **B** (1)

Results and Discussion

The regioselectivity of the reaction was initially tested by reacting (trimethylacetyl)ethynyliodonium triflate (**I**) with 1,3-pentadiene to form a Diels−Alder adduct, 1-(trimethylacetyl-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-methyl-1,4-cyclohexadiene (**3**). The reaction occurred, *vide infra*, with the formation of a single regioisomer, within the detection limits of NMR spectroscopy. The product of the reaction was identified via ^{1}H and ^{13}C NMR, IR, elemental analysis, high-resolution mass spectrometry, and X-ray crystal analysis. The structure of the regioselectively formed isomer was unambiguously determined by single-crystal X-ray analyses of **3** (Tables 1−3 and Figure 1). The reaction shows complete regio-

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[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1997.

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S0022-3263(97)00651-8 CCC: $14.00

Table 1. Crystallographic Data for 3

mol form	$C_{19}H_{22}O_4SIF_3$
mol wt (g/mol)	530.348
space group	$Pna2_1$
space group no.	33
crystal system	orthorhombic
cell constants	
a	12.473(3) Å
b	19.390(3) Å
c	9.072(2) Å
cell volume	2194.06 Å^3
z	4
calcd density (g/cm^3)	1.605
crystal dimens (mm)	0.41 × 0.38 × 0.22
absorption coeff (μ)	15.779 cm^{-1}
radiation (Å)	0.710 73 (Mo K_α)
no. of unique reflcts	1731
no. of reflcts measd	2235
2θ range (deg)	4.00−50.00
scan technique	$\theta/2\theta$
scan width deg	$0.8000 + 0.3400 \tan \theta$
data coll. position	bisecting, with $\omega = 0$
decay correction (%)	0 anisotropic
absorption correction	empirical
minimum % transmission	81.6154
maximum % transmission	98.4981
average % transmission	0.0954
highest peak in final diff Fourier (e/Å^3)	1.184
weighting scheme	non-poisson contribution
data rejected	$I < 3.00(I)$
data rejected	$\sin(t\theta)/\lambda < 0.0500$
no. of observts	1727
no. of variables	252
data to parameter ratio	6.853
shift to error ratio	0.004
error in an observ. of unit weight	1.6844
R_f	0.0439
R_{wf}	0.0522

Table 2. Bond Distances (in angstroms) of 3[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
I	C1	2.166(8)	C4	C5	1.50(1)
I	C13	2.085(9)	C5	C6	1.52(1)
S	O2	1.407(9)	C5	C12	1.54(1)
S	O3	1.401(9)	C6	C7	1.51(1)
S	O4	1.40(1)	C7	C8	1.52(1)
S	C19	1.79(2)	C8	C9	1.54(2)
F1	C19	1.18(2)	C8	C10	1.53(2)
F2	C19	1.27(2)	C8	C11	1.52(2)
F3	C19	1.42(2)	C13	C14	1.36(1)
O1	C7	1.22(1)	C13	C18	1.39(1)
C1	C2	1.48(1)	C14	C15	1.38(2)
C1	C6	1.32(1)	C15	C16	1.40(2)
C2	C3	1.46(2)	C16	C17	1.39(3)
C3	C4	1.30(1)	C17	C18	1.32(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Bond Angles (in degrees) of 3[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C1	I	C13	96.3(3)	C6	C7	C8	124.3(8)
O2	S	O3	118.3(7)	C7	C8	C9	107.7(9)
O2	S	O4	112.3(8)	C7	C8	C10	112.1(9)
O2	S	C19	103.2(8)	C7	C8	C11	110.1(8)
O3	S	O4	111.5(9)	C9	C8	C10	109.0(9)
O3	S	C19	103.9(5)	C9	C8	C11	108.0(1)
O4	S	C19	106.(1)	C10	C8	C11	110.0(1)
I	C1	C2	115.4(6)	I	C13	C14	118.8(7)
I	C1	C6	119.3(6)	I	C13	C18	119.5(9)
C2	C1	C6	125.3(8)	C14	C13	C18	122.(1)
C1	C2	C3	112.1(8)	C13	C14	C15	119.(1)
C2	C3	C4	122.8(8)	C14	C15	C16	119.(2)
C3	C4	C5	122.5(9)	C15	C16	C17	119.(1)
C4	C5	C6	111.5(8)	C16	C17	C18	121.(1)
C4	C5	C12	106.9(8)	C13	C18	C17	120.(1)
C6	C5	C12	110.4(8)	S	C19	F1	118.(1)
C1	C6	C5	118.2(7)	S	C19	F2	114.(1)
C1	C6	C7	120.0(8)	S	C19	F3	105.(1)
C5	C6	C7	121.7(7)	F1	C19	F2	115.(2)
O1	C7	C6	116.8(8)	F1	C19	F3	102.(1)
O1	C7	C8	118.8(7)	F2	C19	F3	100.(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

selectivity with the formation of a single product with the methyl group in the 5 position next to the ketone (Figure 1, isomer **A**, eq 1). Two possible factors can be considered in determining the source of the regioselectivity: electronic and steric effects.

Frontier molecular orbital theory has been used to explain the regioselectivity observed in Diels−Alder reactions with excellent success.[9] According to frontier molecular orbital theory, normal electron demand Diels−Alder reactions depend on the energy difference between the highest occupied molecular orbital (HOMO) of the diene and the lowest unoccupied molecular orbital (LUMO) of the dieneophile. The smaller the energy separation between the orbitals, the more readily the reaction proceeds. Electron-donating substituents on the diene in a normal Diels−Alder reaction facilitate the reaction by raising the energy level of the highest occupied molecular orbital, thereby decreasing the energy separation between the HOMO of the diene and LUMO of the dienophile. Likewise, electron-withdrawing substituents in the dienophile will favor the reaction by lowering the energy of the LUMO. The relative electron densities on the alkynyliodonium can be determined in a qualitative fashion using ^{13}C NMR and experimental observations.[10] The chemical shift of the carbon β to the iodonium is considerably further downfield than the carbon α to the iodonium, suggesting that electron density on the β carbon is less than that of the α carbon. Further evidence can be seen in the reaction of the corresponding alkynyl(phenyl)iodonium salts with nucleophiles. Reactions with a number of nucleophiles have been shown to result in the attack of the carbon β to the iodonium moiety and proceed with the formation of an alkylidene carbene that subsequently rearranges or undergoes carbene insertion reactions.[11] Thus it is reasonable to assume that the iodonium moiety is more electron-withdrawing than the ketone, resulting in a larger coefficient in the LUMO on the carbon β to the iodonium. This analysis would thus predict the regiochemistry to be the 6 substituted product, **B** (eq 1).

In considering the reaction of alkynyl(phenyl)iodonium salts with substituted 1,3-dienes, qualitative analysis with simple modeling would predict that the phenyl group attached to the iodine would be too far removed to provide any significant steric interactions. A bulky functional group on the acetylene, while a fairly remote moiety, should be the most sterically demanding, thus predicting a 6 substituted product, **B** (eq 1) which is the same product predicted by the electronic argument.

The reaction of (trimethylacetyl)ethynyliodonium triflate (**I**) resulted in the formation of isomer **A** (eq 1),

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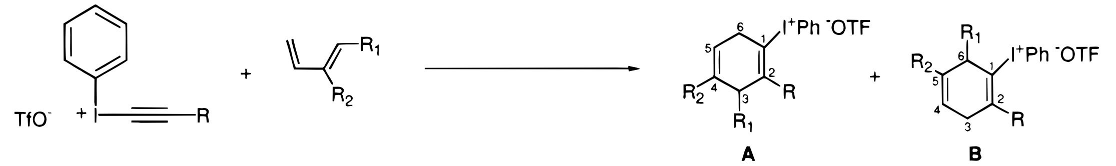
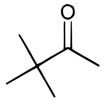
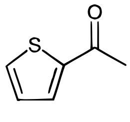
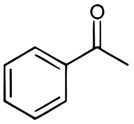
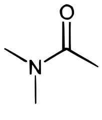
[9] Fleming I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976.

[10] Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH: New York, 1992; p 7.

[11] (a) Stang, P. J.; Crittell, C. M. *J. Org. Chem.* **1992**, *48*, 4305−4306. (b) Fischer, D. R.; Williamson, B. L.; Stang, P. J. *Synlett* **1992**, 535−536. (c) Stang, P. J. *Izv. An SSSR, Ser Khim.* **1993**, 20. (d) Murch, P.; Williamson, B. L.; Stang, P. J. *Synthesis* **1994**, 1255.

Table 4. Cyclization Yields and Product Ratios



	R=	R1=H, R2=Me	R1=H, R2=Me3C	R1=Me, R2=H	R1=Et, R2=H
I		**1** A B 62% 2.6 1	**2** A B 81% 3 1	**3** A 76% 1	**4** A 79% 1
II		**5** A B 65% 9 1	**6** A B 62% 1.3 1	**7** A B 68% 13 1	**8** A B 72% 4.5 1
III		**9** A B 70% 3.4 1	**10** A B 78% 1.3 1	**11** A B 84% 7.3 1	**12** A 79% 1
IV		——	**13** A B 66% 1.4 1	**14** A 73% 1	**15** A B 81% 10 1
V	CN	——	**16** A B 66% 1.1 1	**17** A 72% 1	**18** A B 83% 3 1

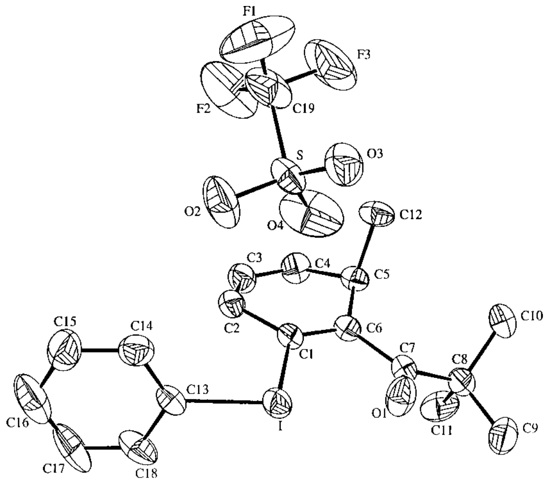


Figure 1. ORTEP of cycloadduct **3**.

which is not the isomer predicted by both electronic and steric arguments. Even though the regioisomer is not the product predicted, the formation of a single regioisomer shows good synthetic promise and other possible explanations can be considered. One clue to the source of the regioselectivity is in the X-ray analysis (Figure 1), which shows an interaction between the ketone oxygen and the positively charged iodine atom, in which electron density is donated from a lone pair on the ketone oxygen into empty orbitals of the positively charged iodine. This is evidenced by the intermolecular distance of the oxygen and the iodine (2.57 Å) being substantially less than the van der Waals radii (3.5 Å), giving orbital overlap. This interaction could provide clues to the observed regiochemisty. In addition, the Diels−Alder reaction has been shown to display a number of subtle nuances. One of these characteristics has been addressed in the Alder rule. The rule is based upon the observation that the Diels−Alder reaction using substrates with unsaturated substituents react preferentially in an endo transition state. Woodward and Hoffmann address this phenomenon at some length and have ascribed it to secondary orbital overlap.[12] Secondary orbital overlap is basically an interaction of spectator substituent orbitals aligning with diene orbitals of similar symmetry and creating a slight stabilizing effect upon the transition state. The selectivity observed in the Diels−Alder reaction of alkynyliodonium salts could be the result of a secondary orbital interaction of the terminal unsubstituted vinyl carbon−carbon double bond and the orbitals of the positively charged iodine atom.

In order to determine if the regiochemistry of this reaction was representative of Diels−Alder reactions of this type, the reactions of a number of other alkynyl(phenyl)iodonium salts (**I-V**) with variously-substituted butadienes were performed under identical reaction conditions. Diels−Alder products were formed only from alkynyliodonium salts bearing electron-withdrawing substituents *β* to the iodonium moiety. The treatment of alkynyl(phenyl)iodonium salts with electron deficient dienes resulted in noncycloaddition reaction pathways or no reaction. Dienes bearing reactive electron rich functional groups were found to participate in Diels−Alder

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[12] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; VCH: New York, 1989.

reactions with alkynyliodonium salts but were not investigated due to the nucleophilic nature and leaving group ability of the substituents.

Butadienes substituted at the one and two positions were investigated to determine the effects of steric interactions on the resulting regiochemistry (Table 4). Terminally substituted butadienes were of particular interest since they show a higher degree of polarized electron distribution and have the potential for more demanding steric interactions. Methyl- and ethyl-substituted butadienes were compared to minimize the differences to steric considerations only. The reaction of 1,3-pentadiene with alkynyl(phenyl)iodonium salts resulted in the formation of a single regioisomer in three out of five cases (**3**, **14**, **17**). Ratios of 13:1 and 7.3:1 were observed in the remaining two cases (Table 4).

The reaction of alkynyliodonium salts with 1,3-hexadiene also resulted in good selectivity (Table 4). The relative steric demand of the ethyl group is only slightly higher than that of the methyl group but can affect the regiochemistry. In the case of the thiofuroyl (**II**), dimethylcarbamoyl (**IV**), and cyano (**V**) functionalized ethynyl(phenyl)iodonium salts, the slight loss of some regioselectivity was observed, probably due to the slightly increased steric demand.

2-Substituted butadienes are also unsymmetrical and have similar electron configurations, but have a different steric effect on the resulting regiochemistry. The reaction of keto-substituted alkynyl(phenyl)iodonium salts with 2-methylbutadiene (isoprene) resulted in Diels−Alder products showing only low selectivity. The thiofuroylalkynyl(phenyl)iodonium salt (**II**) displayed the best selectivity of 9:1 with the preferred product bearing the methyl group in the 4 position (*vide infra*) (eq 1, **A**). The (trimethylacetyl)ethynyl (**I**) and benzoylethynyl (**III**) iodonium salts show only limited selectivity of 2.6:1 and 3.4:1, respectively. The reactions of dimethylcarbamoyl (**IV**) and cyano (**V**) functionalized alkynyl(phenyl)iodonium salts with isoprene occur slowly with the formation of side products, making the isolation of the desired product unattainable.

In an effort to determine whether the low observed selectivity was arising from a steric effect, a larger substituent was used: 2-*tert*-butylbutadiene. The electronic distribution of 2-*tert*-butylbutadiene is the same as in isoprene. The resulting products showed a loss of regioselectivity compared to the isoprene case. This selectivity displayed a range from none, in the case of the cyanoethynyl(phenyl)iodonium salt (**V**), to 3:1 ratio for the (trimethylacetyl)ethynyl(phenyl)iodonium salt (**I**). Reaction of the more sterically demanding diene resulted in a loss of regioselectivity in all cases with the exception of a very slight increase in the case of the (trimethylacetyl)ethynyl(phenyl)iodonium salt. This data suggests that the nature of the substituent at the 2 position of the diene does have a steric affect on the selectivity of the reaction: the reaction with 2-methylbutadiene results in a slight preference for the formation of 4-substituted cyclohexadienes while with 2-*tert*-butylbutadiene there is no preference (Table 4).

These results show that steric interactions at the 2 position do not contribute as significantly to regioselective reactions while substituents on the 1 position enable nearly complete selectivity. Electronic interactions are important to the extent that electron rich dienes participate in the Diels−Alder reaction of alkynyliodonium salts while electron deficient dienes do not.

The regioconnectivity of all other products is based upon analogy of the ^{1}H NMR with product **3** and the known regiochemistry as determined by X-ray structural analysis (*vide infra*). The ^{1}H NMR spectra of product **3** shows a broad signal corresponding to one proton centered at δ 3.91, which is the proton at the 3 position, and a signal for two protons as a broad multiplet at δ 3.00 corresponding to the protons at the 6 position. The highly split and broad nature of these signals can be explained as a result of cross ring splitting and inequivalence of the geminal protons in this nearly planar system. The downfield chemical shift of the proton at the 3 position of the ring is consistent with the polarization observed in previously reported vinyliodonium systems. Two signals corresponding to the vinyl protons appear as broad multiplets at δ 5.57 (5 position) and δ 5.92 (4 position). Connectivity for other products were determined by analogy on the basis of similar proton NMR data. All of the spectra are consistent with the major regio-product being analogous to product **3**. The NMR for all of the 3-substituted ring systems have similar chemical shifts for the single proton at the 3 position between δ 3.55−4.16 and δ 2.99−3.42 for the two protons at the 6 position. The spectra for the 4-substituted ring systems are consistent with the observations seen in the 3-substituted analogs. The reaction of isoprene with the (trimethylacetyl)ethynyl(phenyl)alkynyliodonium salt (**I**) produces two regioproducts in a 2.6:1 ratio mixture (**1a,b**). The major product shows ^{1}H NMR signals at δ 3.60, 5.58, and 2.73. These signals correspond to the protons at the 3, 4, and 5 positions, respectively, and the minor product shows similar signals at δ 3.52, 5.22, and 2.82 corresponding to the protons at the 3, 5, and 6 positions (eq 1). This data corresponds closely to the major product having the same substitution pattern as product **3** and the minor product having the opposite configuration. The other products resulting from the reaction with the 2-substituted dienes were likewise identified.

X-ray Crystallography

The regioselectivity of these reactions was unambiguously determined by single-crystal X-ray analyses of product **3** (Tables 1−3 and Figure 1), resulting from the reaction of 1,3-pentadiene with a trimethylacetyl-substituted alkynyl(phenyl)iodonium salt (**I**). A suitable crystal was grown from a solution of methylene chloride using vapor diffusion of hexanes at low temperature. The cyclohexadiene shows normal carbon−carbon double-bond distances of 1.30 and 1.32 Å and a carbon−iodine bond distance of 2.16 Å. The triflate oxygens are 3.72, 4.31, and 5.15 Å, well outside the overlap of the van der Waals radii of 3.5 Å, showing that the triflate ionically bonded. The ketone oxygen is 2.57 Å distant from the iodine which is within the 3.5 Å maximum distance for a dative interaction. This interaction produces a five-membered ring containing the iodonium, carbon−carbon double bond, and the ketone. The X-ray structure of product 3 shows a C1−I−C13 bond angle of 96.3° which follows the predicted geometry. The C1−I−O1 bond angle is 71° which places the iodine atom in a distorted T-shaped geometry which is characteristic of iodonium salts.[11]

Conclusions

Acetylenes have been utilized in Diels−Alder reactions but have been limited by the need for harsh conditions that limit the functionality that can be incorporated. The incorporation of an iodonium moiety as an activating group on acetylenes has allowed the use of mild conditions and the incorporation of a number of functional groups. Further, the iodonium moiety allows for subsequent elaboration of the resulting products. This study of the Diels−Alder cycloaddition chemistry of alkynyl(phenyl)iodonium salts has found that they show low regioselectivity in the case of 2-substituted dienes, display a good degree of regioselectivity, and are regiospecific in the case of 1-substituted dienes. The resultant regioselectivity, as proven by single-crystal X-ray analysis, is counterintuitive when considering electronic and steric concerns and is a likely result of secondary orbital overlap.

Experimental Section

General Methods. Infrared spectra were recorded neat or as CCl_4 mulls on a Mattson FT-IR spectrometer. All NMR spectra were recorded on a Unity 300 Varian spectrometer or a VXR-500 Varian spectrometer. The ^1H NMR spectra were recorded at 300 MHz, and chemical shifts are reported relative to $CDCl_3$ δ 7.24, CD_2Cl_2 δ 5.32, or CD_3CN δ 1.93. The ^{13}C NMR spectra were recorded at 75 MHz or 125 MHz, ^1H decoupled, and reported relative to $CDCl_3$ δ 77.0, CD_2Cl_2 δ 53.24, or CD_3CN δ 1.30. The ^{19}F NMR spectra were recorded at 282 MHz, and chemical shifts were reported relative to external $CFCl_3$ (sealed capillary) in the appropriate deuterated solvent.

Mass spectra were obtained with a Finnigan MAT 95 mass spectrometer with a Finnigan MAT ICIS II operating system under positive ion fast atom bombardment (FAB) conditions at 8 keV. 3-Nitrobenzyl alcohol was used as a matrix in CH_2Cl_2, $CHCl_3$, or CH_3CN as solvent. Poly(propylene glycol) was used as a reference for peak matching. X-ray data was collected on a Enraf-Nonius CAD4 diffractometer. The structure was solved by standard heavy atom techniques with the SDP/VAX package. Non-hydrogen atoms were refined with anisotropic thermal parameters. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

Materials. All commercial reagents were ACS reagent grade and used without further purification. Reagent grade methylene chloride, hexanes, and acetonitrile were dried by distillation over CaH_2. Diethyl ether and THF were distilled from Na/benzophenone. Reaction flasks were flame-dried and flushed with nitrogen prior to use. Isoprene, 1,3-pentadiene, and hexadiene were purchased from Aldrich as mixtures of *cis* and *trans* isomers and distilled prior to use. 2-(Dimethylethyl)-1,3-butadiene was prepared according to a literature procedure.[13] The syntheses of alkynyliodonium triflates have been previously reported.[6]

1-(Trimethylacetyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-5-methyl-1,4-cyclohexadiene (1a and 1b). To a stirred solution of (trimethylacetyl)ethynyl(phenyl)iodonium triflate (0.15 g, 0.32 mmol) in 5 mL of CH_3CN at 20 °C under nitrogen was added isoprene (0.2 mL, excess) dropwise, and the solution was stirred for 3 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting oil was crystallized from CH_3CN/diethyl ether/hexanes affording 0.107 g (62%) of an inseparable mixture of two isomers (2.6:1) as a white microcrystalline solid: ^1H NMR (CD_2Cl_2) δ 8.04 (t, 2H, J = 7.5 Hz), 7.81 (t, 1H, J = 7.5 Hz), 7.60 (t, 2H, J = 7.2 Hz), 5.58 (m, 1H), 3.60 (m, 2H), 2.73 (t, 2H, J = 8.1 Hz), 1.38 (s, 3H), 1.17 (s, 9H); ^{19}F NMR (CD_2Cl_2) δ −76.1 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_2Cl_2) δ 195.2, 142.6, 142.5, 142.1, 139.8, 138.1, 138.0, 136.5, 134.9, 134.8, 134.5, 132.7, 132.1, 125.3, 121.3, 114.5, 114.4, 50.1, 49.4, 43.9, 43.5, 38.3, 37.6, 31.66, 31.64; IR (CCl_4) 2944, 2933, 2116, 1733, 1635, 1617, 1472, 1464, 1457, 1439, 1293, 1227, 1168 cm^{-1}; FAB HRMS m/z calcd for $C_{18}H_{22}OI$ (M − $CF_3SO_4^-$) 381.07070, found 381.07154.

1-(Trimethylacetyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-5-(dimethylethyl)-1,4-cyclohexadiene (2a and 2b). To a stirred solution of (trimethylacetyl)ethynyl(phenyl)iodonium triflate (0.10 g, 0.22 mmol) in 5 mL of CH_3CN at 20 °C under nitrogen was added 2-(dimethylethyl)-1,3-butadiene (0.2 mL, excess) dropwise, and the solution was stirred for 3 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL). The resulting oil was crystallized from CH_3CN/diethyl ether/hexanes affording 0.10 g (81%) of an inseparable mixture of two isomers (4:1) as a white microcrystalline solid: ^1H NMR ($CDCl_3$) δ 8.10 (t, 2H, J = 7.5 Hz), 7.71 (t, 1H, J = 7.8 Hz), 7.52 (d, 2H, J = 7.8 Hz), 5.55 (br s, 1H), 3.58 (m, 2H), 2.72 (t, 2H, J = 7.2 Hz), 1.33 (s, 9H), 0.74 (s, 9H); ^{19}F NMR ($CDCl_3$) δ -76.3 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 206.2, 141.8, 136.0, 133.2, 131.6, 129.8, 127.8, ($CF_3SO_3^-$ not observed), 113.6, 110.4, 45.2, 35.5, 34.9, 32.9, 28.1, 26.8; IR (CCl_4) 2962, 1685, 1647, 1284, 1272, 1249, 1181, 1070 cm^{-1}, Anal. Calcd for $C_{22}H_{28}O_4SF_3I$: C, 46.16; H, 4.93; S, 5.6. Found: C, 45.48; H, 4.87; S, 5.53.

1-(Trimethylacetyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-methyl-1,4-cyclohexadiene (3). To a stirred solution of (trimethylacetyl)ethynyl(phenyl)iodonium triflate (0.20 g, 0.43 mmol) in 10 mL of CH_3CN at 20 °C under nitrogen was added 1,3-pentadiene (0.3 mL, excess) dropwise, and the solution was stirred for 2 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL). The resulting oil was crystallized from CH_2Cl_2/hexanes affording 0.174 g (76%) as a tan microcrystalline solid, mp 132−134 °C dec: ^1H NMR (CD_2Cl_2) δ 8.05 (d, 2H, J = 8.1 Hz), 7.78 (t, 1H, J = 7.2 Hz), 7.59 (t, 2H, J = 8.7 Hz), 5.92 (br m, 1H), 5.57 (br m, 1H), 3.91 (m, 1H), 3.00 (br m, 2H), 1.38 (s, 9H), 1.19 (d, 3H, J = 6.9 Hz); ^{19}F NMR (CD_2Cl_2) δ −79.2 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_2Cl_2) δ 211.3, 148.3, 137.7, 133.9, 132.6, 129.3, 122.3, ($CF_3SO_3^-$ not observed), 109.4, 67.5, 45.5, 37.2, 35.2, 27.4, 22.9; IR (CCl_4) 2963, 1683, 1281, 1235, 1168, 1025 cm^{-1}. Anal. Calcd for $C_{19}H_{22}O_4SF_3I$: C, 43.03; H, 4.18; S, 6.05. Found: C, 43.09; H, 4.25; S, 6.0. FAB HRMS: m/z calcd for $C_{18}H_{22}OI$ (M − $CF_3SO_4^-$) 381.07032, found 381.07142.

1-(Trimethylacetyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-ethyl-1,4-cyclohexadiene (4). To a stirred solution of (trimethylacetyl)ethynyl(phenyl)iodonium triflate (0.10 g, 0.22 mmol) in 5 mL of CH_3CN at 20 °C under nitrogen was added 1,3-hexadiene (0.1 mL, excess) dropwise, and the solution was stirred for 2 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting oil was crystallized from CH_2Cl_2/hexanes affording 0.093 g (79%) as a tan microcrystalline solid: ^1H NMR ($CDCl_3$) δ 8.07 (d, 2H, J = 7.5 Hz), 7.70 (t, 1H, J = 7.5 Hz), 7.53 (t, 2H, J = 8.1 Hz), 5.83 (br m, 1H), 5.66 (br m, 1H), 3.79 (m, 1H), 3.05 (br m, 2H), 1.34 (br m, 11H), 0.785 (t, 3H, J = 7.5 Hz); ^{19}F NMR ($CDCl_3$) δ −75.7 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 198.1, 138.0, 134.4, 133.0, 130.8, 127.5, 124.1, 122.4, ($CF_3SO_3^-$ not observed), 109.1, 45.8, 43.4, 35.6, 30.2, 27.6, 9.7; IR (CCl_4) 2970, 1684, 1559, 1472, 1462, 1457, 1283, 1257, 1244, 1165, 1028 cm^{-1}; FAB HRMS m/z calcd for $C_{19}H_{24}OI$ (M − $CF_3SO_4^-$) 395.08372, found 395.08707.

1-(2-Thiofuroyl)-2-[(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-5-methyl-1,4-cyclohexadiene (5a and 5b). To a stirred solution of (2-thiofuroylethynyl)(phenyl)iodonium triflate (0.25 g, 0.51 mmol) in 10 mL of CH_3CN at 20 °C under nitrogen was added isoprene (0.5 mL, excess) dropwise, and the solution was stirred for 3 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL). The resulting solid was recrystallized from CH_2Cl_2/diethyl ether affording 0.18 g (65%) of an inseparable mixture of two isomers (9:1) as a white microcrystalline solid: ^1H NMR (CD_2Cl_2) δ 8.15 (d, 1H, J = 4.2 Hz), 8.09 (d, 2H, J = 7.2 Hz), 8.01 (d, 1H, J = 7.8 Hz), 7.78 (t, 1H, J = 7.5 Hz), 7.60 (t, 2H, J = 7.8 Hz), 7.32 (t, 1H, J = 4.5 Hz), 5.66 (m, 1H), 3.80 (br m, 2H), 2.80 (t, 2H, J = 8.4 Hz), 1.57 (s, 3H); ^{19}F NMR (CD_2Cl_2) δ −75.3 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_2Cl_2) δ 184.4, 140.1, 139.4, 138.2, 137.8, 134.8, 134.0, 132.3, 130.4, 129.9, 129.1, ($CF_3SO_3^-$ not observed), 117.1, 110.3, 39.6, 34.1,

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(13) Bartlett, P. D.; Wallbillich, G. E. H.; Wingrove, A. S.; Swenton, J. S.; Montgomery, L. K.; Kramer, B. D. *J. Am. Chem. Soc.* **1968**, *90*, 2049. See also: Backer, H. J.; Strating, J. *Recl. Trav. Chim.* **1934**, *53*, 525.

21.9; IR (CCl_4) 3090, 2912, 1622, 1279, 1246, 1217, 1157 cm^{-1}; FAB HRMS m/z calcd for $C_{18}H_{16}SOI$ ($M - CF_3SO_3^-$) 406.9966, found 406.9965.

1-(2-Thiofuroyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-5-(dimethylethyl)-1,4-cyclohexadiene (6a and 6b). To a stirred solution of (2-thiofuroylethynyl)(phenyl)iodonium triflate (0.10 g, 17 mmol) in 5 mL of CH_3CN at 20 °C under nitrogen was added 2-(dimethylethyl)-1,3-butadiene (0.1 mL, excess) dropwise, and the solution was stirred for 3 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL). The resulting solid was recrystallized from CH_2Cl_2/diethyl ether affording 0.076 g (62%) of an inseparable mixture of two isomers (1.3:1) as a white microcrystalline solid: ^{1}H NMR ($CDCl_3$) δ 8.21 (d, 1H, $J = 3.9$ Hz), 8.10 (m, 3H), 7.83 (q, 1H, $J = 8.1$ Hz), 7.63 (q, 2H, $J = 7.8$ Hz), 7.35 (q, 1H, $J = 4.8$ Hz), 5.74 (br m, 1H), 5.42 (br m, 1H), 3.82 (t, 2H, $J = 8.4$ Hz), 2.88 (m, 2H), 1.10 (s, 9H), 1.08 (s, 9H); ^{19}F NMR ($CDCl_3$) δ −76.3 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 196.1, 195.6, 154.1, 153.4, 151.7, 151.4, 151.0, 150.8, 149.7, 149.6, 149.3, 147.0, 145.7, 145.5, 145.4, 143.8, 143.7, 142.2, 142.0, 141.5, 141.5, 140.7, 126.0, 125.6, 122.3, 121.9, ($CF_3SO_3^-$ not observed), 47.7, 46.9, 46.8, 45.7, 45.1, 40.4, 39.9; IR (CCl_4) 2966, 2947, 1625, 1578, 1407, 1351, 1272, 1247, 1160, 1152 cm^{-1}; FAB HRMS m/z calcd for $C_{18}H_{16}SOI$ ($M - CF_3SO_3^-$) 449.03971, found 449.04349.

1-(2-Thiofuroyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-methyl-1,4-cyclohexadiene (7a and 7b). To a stirred solution of (2-thiofuroylethynyl)(phenyl)iodonium triflate (0.49 g, 1.0 mmol) in 10 mL of CH_3CN at 20 °C under nitrogen was added 1,3-pentadiene (0.5 mL, excess) dropwise, and the solution was stirred for 4 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL). The resulting solid was recrystallized from CH_2Cl_2/hexanes affording 0.37 g (68%) of an inseparable mixture of two isomers (13:1) as a tan microcrystalline solid: ^{1}H NMR ($CDCl_3$) δ 8.06 (m, 4H), 7.78 (t, 1H, $J = 7.8$ Hz), 7.59 (t, 2H, $J = 7.8$ Hz), 7.31 (t, 1H, $J = 4.5$ Hz), 5.88 (m, 1H), 5.57 (m, 1H), 4.14 (m, 1H), 3.05 (m, 2H), 1.23 (d, 3H, $J = 7.2$ Hz); ^{19}F NMR ($CDCl_3$) δ −76.3 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 186.4, 143.4, 139.7, 138.9, 137.9, 137.1, 133.9, 132.5, 129.9, 129.3, 126.6, 121.3, ($CF_3SO_3^-$ not observed), 109.8, 38.4, 35.5, 22.1; IR (CCl_4) 3053, 2969, 1680, 1557, 1272, 1250, 1222, 1088 cm^{-1}; FAB HRMS m/z calcd for $C_{18}H_{16}SOI$ ($M - CF_3SO_4^-$) 406.9973, found 406.9965.

1-(2-Thiofuroyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-ethyl-1,4-cyclohexadiene (8a and 8b). To a stirred solution of (2-thiofuroylethynyl)(phenyl)iodonium triflate (0.10 g, 0.20 mmol) in 5 mL of CH_3CN at 20 °C under nitrogen was added 1,3-hexadiene (0.05 mL, excess) dropwise, and the solution was stirred for 2 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL). The resulting solid was recrystallized from CH_2Cl_2/hexanes affording 0.084 g (72%) of an inseparable mixture of two isomers (4.5:1) as a tan microcrystalline solid: ^{1}H NMR (CD_2Cl_2) δ 8.0 (m, 3H), 7.8 (d, 1H, $J = 6.0$ Hz), 7.74 (t, 2H, $J = 7.2$ Hz), 7.3 (t, 1H $J = 4.5$ Hz), 5.87 (m, 1H), 5.67 (m, 1H), 4.16 (m, 1H), 2.99 (m, 2H), 1.62 (br m, 2H), 0.92 (t, 3H $J = 7.5$Hz), 0.82 (t, 3H $J = 7.5$); ^{19}F NMR (CD_2Cl_2) δ −76.2 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_2Cl_2) δ 186.9, 139.9, 139.0, 138.1, 137.9, 137.2, 134.1, 132.7, 130.8, 130.0, 127.4, 123.1, ($CF_3SO_3^-$ not observed), 109.8, 44.4, 35.8, 28.7, 9.6; IR (CCl_4) 2968, 2933, 2876, 1676, 1623, 1559, 1472, 1408, 1354, 1276, 1244, 1224, 1163 cm^{-1}; FAB HRMS m/z calcd for $C_{19}H_{18}SOI$ ($M - CF_3SO_4^-$) 421.01467, found 421.01219.

1-Benzoyl-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-5-methyl-1,4-cyclohexadiene (9a and 9b). To a stirred solution of benzoylethynyl(phenyl)iodonium triflate (0.10 g, 0.21 mmol) in 5 mL of CH_3CN at 20 °C under nitrogen was added isoprene (0.2 mL, excess) dropwise, and the solution was stirred for 3 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting oil was crystallized from CH_3CN/diethyl ether/hexanes affording 0.080 g (70%) of an inseparable mixture of two isomers (3.4:1) as a white microcrystalline solid: ^{1}H NMR (CD_2Cl_2) δ 8.11 (m, 2H), 7.69 (m, 8H), 5.55 (br m, 1H), 3.45 (m, 2H), 2.86 (m, 2H), 1.69 (s, 3H), 1.57 (s, 3H); ^{19}F NMR (CD_2Cl_2) δ −76.4 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_2Cl_2) δ 196.9, 138.6, 136.7, 135.7, 134.5, 134.2, 132.6, 130.6, 129.4, 129.3, 128.1,($CF_3SO_3^-$ not observed), 117.7, 109.3, 39.7, 35.1, 22.2; IR (CCl_4) 3069, 1650, 1573, 1472, 1443, 1260, 1172, 1029 cm^{-1}; FAB HRMS m/z calcd for $C_{28}H_{18}OI$ ($M - CF_3SO_4^-$) 401.04162, found 401.04012.

1-Benzoyl-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-5-(dimethylethyl)-1,4-cyclohexadiene (10a and 10b). To a stirred solution of benzoylethynyl(phenyl)iodonium triflate (0.10 g, 0.21 mmol) in 4 mL of CH_3CN at 20 °C under nitrogen was added 2-(dimethylethyl)-1,3-butadiene (0.1 mL, excess) dropwise, and the solution was stirred for 4 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting product oiled out of CH_3CN/diethyl ether/hexanes affording 0.96 g (78%) of an inseparable mixture of two isomers (1.3:1) as a yellow viscous oil: ^{1}H NMR ($CDCl_3$) δ 8.09 (m, 2H), 7.61 (m, 8H), 5.54 (br m, 1H), 5.31 (br m, 1H), 3.39 (m, 2H), 2.96 (m, 1H), 2.85 (m, 1H), 0.951 (s, 9H), 0.79 (s, 9H); ^{19}F NMR ($CDCl_3$) δ −74.6 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 196.5, 196.0, 143.0, 142.2, 138.1, 138.0, 137.5, 136.0, 135.5, 135.3, 134.1, 133.9, 133.6, 133.5, 132.1, 132.0, 129.1, 129.0, 127.5, ($CF_3SO_3^-$ not observed), 114.4, 109.7, 109.4, 35.9, 35.3, 35.2, 34.9, 34.3, 34.6, 33.8, 28.8, 28.5; IR (CCl_4) 3064, 2966, 1681, 1597, 1568, 1474, 1444, 1278, 1224, 1155, 1028 cm^{-1}; FAB HRMS m/z calcd for $C_{23}H_{24}OI$ ($M - CF_3SO_4^-$) 443.089251, found 443.087067.

1-Benzoyl-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-methyl-1,4-cyclohexadiene (11a and 11b). To a stirred solution of benzoylethynyl(phenyl)iodonium triflate (0.10 g, 0.43 mmol) in 10 mL of CH_3CN at 20 °C under nitrogen was added 1,3-pentadiene (0.1 mL, excess) dropwise, and the solution was stirred for 3 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting oil was crystallized from CH_2Cl_2/hexanes affording 0.096 g (84%) of an inseparable mixture of two isomers (7.3:1) as a tan microcrystalline solid: ^{1}H NMR (CD_2Cl_2) δ 8.08 (d, 2H, $J = 7.2$ Hz), 7.76 (m, 4H), 7.59 (m, 4H), 5.81 (br m, 1H), 5.55 (br m, 1H), 3.88 (m, 1H), 3.01 (q, 2H), 1.37 (d, 3H, $J = 6.9$), 0.96 (d, 3H, $J = 6.9$ Hz); ^{19}F NMR ($CDCl_3$) δ −75.9 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_2Cl_2) δ 197.7, 143.8, 138.2, 135.5, 134.9, 134.2, 132.7, 129.7, 129.4, 129.2, 126.8, 121.4, ($CF_3SO_3^-$ not observed), 109.0, 39.0, 35.5, 21.7; IR (CCl_4) 2964, 1678, 1663, 1596, 1576, 1568, 1472, 1445, 1275, 1157, 1027 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_4SF_3I$: C, 45.83; H, 3.30; S, 5.83. Found: C, 45.68; H, 3.27; S, 5.57.

1-Benzoyl-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-ethyl-1,4-cyclohexadiene (12). To a stirred solution of benzoylethynyl(phenyl)iodonium triflate (0.10 g, 0.22 mmol) in 5 mL of CH_3CN at 20 °C under nitrogen was added 1,3-hexadiene (0.1 mL, excess) dropwise, and the solution was stirred for 2 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting oil was crystallized from CH_2Cl_2/hexanes affording 0.093 g (79%) as a white microcrystalline solid, mp 130−133 °C dec: ^{1}H NMR (CD_2Cl_2) δ 8.09 (d, 2H, $J = 7.8$ Hz), 7.77 (m, 4H), 7.59 (m, 4H), 5.80 (br m, 1H), 5.67 (br m, 1H), 3.90 (m, 1H), 3.02 (br m, 2H), 1.36 (br m, 2H), 0.67 (t, 3H, $J = 7.5$ Hz); ^{19}F NMR (CD_2Cl_2) δ −76.3 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_2Cl_2) δ 193.1, 143.6, 138.2, 135.3, 135.1, 134.2, 132.8, 129.7, 129.4, 127.5, 126.3, 123.2, ($CF_3SO_3^-$ not observed), 109.1, 44.8, 35.8, 28.2, 9.5; IR (CCl_4) 3067, 2966, 1644, 1445, 1271, 1224, 1157, 1027 cm^{-1}; FAB HRMS m/z calcd for $C_{21}H_{20}OI$ ($M - CF_3SO_4^-$) 415.05622, found 415.05577.

1-(Dimethylcarbamoyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-5-(dimethylethyl)-1,4-cyclohexadiene (13a and 13b). To a stirred solution of (trimethylacetyl)ethynyl(phenyl)iodonium triflate (0.10 g, 24 mmol) in 5 mL of CH_3CN at 20 °C under nitrogen was added [2-(dimethylethyl)-1,3-butadiene (0.1 mL, excess) dropwise, and the solution was stirred for 10 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting product oiled out of CH_3CN/diethyl ether/hexanes affording 0.083 g (66%) of an inseparable mixture of two isomers (1.4:1) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 8.15 (t, 2H, $J = 8.1$ Hz), 7.65 (m, 1H), 7.51 (m, 2H), 5.54 (br s, 1H), 5.31 (m, 2H), 3.23 (br m, 10H), 1.02 (s, 9H), 0.90 (s, 9H); ^{19}F NMR (CDCl$_3$) δ −76.3 (s, $CF_3SO_3^-$); ^{13}C NMR (CDCl$_3$) δ 143.3, 141.7, 141.5, 137.5, 136.8, 134.4, 132.9, 132.5, 132.0, 132.0, 130.2, 121.3, ($CF_3SO_3^-$ not observed), 119.3, 118.2, 115.3, 113.3, 110.2, 109.9, 35.8, 35.4, 35.2, 34.6, 32.3, 31.3, 28.6, 28.4; IR (CCl$_4$) 3060, 2967, 1616, 1474, 1405, 1283, 1252, 1224, 1156, 1031 cm^{-1}; FAB HRMS *m*/*z* calcd for $C_{19}H_{25}NOI$ (M − $CF_3SO_4^-$) 410.09651, found 410.09797.

1-(Dimethylcarbamoyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-methyl-1,4-cyclohexadiene (14). To a stirred solution of (trimethylacetyl)ethynyl(phenyl)iodonium triflate (0.10 g, 0.24 mmol) in 10 mL of CH$_3$CN at 20 °C under nitrogen was added 1,3-pentadiene (0.1 mL, excess) dropwise, and the solution was stirred for 12 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL). The resulting product oiled out of CH$_2$Cl$_2$/hexanes affording 0.085 g (73%) as a red oil: ^{1}H NMR (CDCl$_3$) δ 8.15 (d, 2H, *J* = 8.1 Hz), 7.67 (t, 1H, *J* = 7.8 Hz), 7.53 (t, 2H, *J* = 7.8 Hz), 5.69 (br m, 1H), 5.49 (br m, 1H), 3.79 (br m, 1H), 3.26 (br m, 2H), 3.12 (s, 6H), 1.20 (d, 3H, *J* = 7.2 Hz); ^{19}F NMR (CDCl$_3$) δ −74.8 (s, $CF_3SO_3^-$); ^{13}C NMR (CDCl$_3$) δ 168.4, 148.7, 136.8, 133.2, 132.4, 128.5, 122.3, ($CF_3SO_3^-$ not observed), 119.7, 109.9, 37.0, 35.5, 21.2; IR (CCl$_4$) 3053, 2973, 1631, 1496, 1472, 1442, 1409, 1397, 1274, 1259, 1167, 1032 cm^{-1}; FAB HRMS *m*/*z* calcd for $C_{16}H_{19}NOI$ (M − $CF_3SO_4^-$) 368.051141, found 368.049897.

1-(Dimethylcarbamoyl)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-ethyl-1,4-cyclohexadiene (15a and 15b). To a stirred solution of (trimethylacetyl)ethynyl(phenyl)iodonium triflate (0.10 g, 0.24 mmol) in 5 mL of CH$_3$CN at 20 °C under nitrogen was added 1,3-hexadiene (0.05 mL, excess) dropwise, and the solution was stirred for 24 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting product oiled out of CH$_2$Cl$_2$/hexanes affording 0.097 g (81%) of an inseparable mixture of two isomers (10:1) as a red oil: ^{1}H NMR (CDCl$_3$) δ 8.12 (d, 2H, *J* = 8.7 Hz), 7.75 (t, 1H, *J* = 7.5 Hz), 7.57 (t, 2H, *J* = 7.8 Hz), 5.73 (br m, 1H), 5.65 (br m, 1H), 3.61 (m, 1H), 3.11 (s, 6H), 3.07 (br m, 1H), 1.61 (br m, 2H), 0.816 (t, 3H, *J* = 7.8 Hz); ^{19}F NMR (CDCl$_3$) δ (s, $CF_3SO_3^-$) −75.5; ^{13}C NMR (CDCl$_3$) δ 168.5, 147.5, 136.9, 133.3, 132.3, 126.4, 124.0, 120.32, ($CF_3SO_3^-$ not observed), 110.0, 42.7, 35.7, 27.5, 27.0, 9.3; IR (CCl$_4$) 2968, 2935, 1635, 1405, 1283, 1246, 1225, 1163, 1029 cm^{-1}; FAB HRMS *m*/*z* calcd for $C_{17}H_{21}NOI$ (M − $CF_3SO_4^-$) 382.06667, found 382.06291.

1-(Cyano)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-5-(dimethylethyl)-1,4-cyclohexadiene (16a and 16b). To a stirred solution of (cyano)ethynyl(phenyl)iodonium triflate (0.10 g, 0.25 mmol) in 5 mL of CH$_3$CN at 20 °C under nitrogen was added 2-(dimethylethyl)-1,3-butadiene (0.1 mL, excess) dropwise, and the solution was stirred for 8 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 10 mL). The resulting product oiled out of CH$_2$Cl$_2$/hexanes affording 0.083 g (66%) of an inseparable mixture of two isomers (1:1) as a pale yellow oil: ^{1}H NMR (CH$_3$CN) δ 8.12 (m, 2H), 7.68 (t, 1H, *J* = 7.5 Hz), 7.52 (t, 2H, *J* = 8.1 Hz), 5.47 (br m, 1H), 5.30 (br m, 1H), 3.60 (m, 2H), 3.24 (m, 2H), 0.99 (s, 9H), 0.97 (s, 9H); ^{19}F NMR (CD$_3$CN) δ −76.3 (s, $CF_3SO_3^-$); ^{13}C NMR (CD$_3$CN) δ 142.8, 140.0, 136.2, 136.0, 133.1, 132.4, 132.4, 131.1, 125.0, 124.3, 114.6, 112.7, 112.5, 111.9, ($CF_3SO_3^-$ not observed), 37.0, 36.0, 35.5, 35.2, 32.2, 31.2, 28.4, 28.3; IR (CCl$_4$) 3065, 2912, 2873, 2261, 1472, 1444, 1419, 1366, 1053 cm^{-1}; FAB HRMS *m*/*z* calcd for $C_{17}H_{19}NI$ (M − $CF_3SO_4^-$) 364.05610, found 364.05717.

1-(Cyano)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-methyl-1,4-cyclohexadiene (17). To a stirred solution of (cyano)ethynyl(phenyl)iodonium triflate (0.10 g, 0.25 mmol) in 10 mL of CH$_3$CN at 20 °C under nitrogen was added 1,3-pentadiene (0.05 mL, excess) dropwise, and the solution was stirred for 8 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL) and then diethyl ether (2 × 5 mL). The resulting oil was crystallized from CH$_2$Cl$_2$/hexanes affording 0.084 g (72%) as a tan microcrystalline solid, mp 114−115 °C dec: ^{1}H NMR (CDCl$_3$) δ 8.13 (d, 2H, *J* = 7.8 Hz), 7.76 (t, 1H, *J* = 7.5 Hz), 7.59 (t, 2H, *J* = 8.1 Hz), 5.70 (d, 1H, *J* = 9.9 Hz), 5.55 (d, 1H, *J* = 10.0 Hz), 3.55 (m, 2H), 3.38 (m, 1H), 1.36 (d, 3H, *J* = 7.2 Hz); ^{19}F NMR (CD$_2$Cl$_2$) δ −79.1 (s, $CF_3SO_3^-$); ^{13}C NMR (CD$_2$Cl$_2$) δ 136.4, 133.8, 133.0, 131.9, 130.3, 127.4, 121.6, ($CF_3SO_3^-$ not observed), 117.6, 112.5, 37.1, 36.5, 21.0; IR (CCl$_4$) 2922, 2224, 1281, 1235, 1168, 1025 cm^{-1}; FAB HRMS *m*/*z* calcd for $C_{14}H_{13}NI$ (M − $CF_3SO_4^-$) 322.0091, found 322.0105.

1-(Cyano)-2-(phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo)-6-ethyl-1,4-cyclohexadiene (18a and 18b). To a stirred solution of (cyano)ethynyl(phenyl)iodonium triflate (0.10 g, 0.25 mmol) in 5 mL of CH$_3$CN at 20 °C under nitrogen was added 1,3-hexadiene (0.1 mL, excess) dropwise, and the solution was stirred for 24 h. The solvent was removed using a rotary evaporator and the product washed with hexanes (2 × 5 mL). The resulting oil was crystallized from CH$_3$CN/diethyl ether/hexanes affording 0.10 g (83%) of an inseparable mixture of two isomers (3:1) as a white microcrystalline solid: ^{1}H NMR (CD$_2$Cl$_2$) δ 8.12 (d, 2H, *J* = 7.5 Hz), 7.76 (t, 1H, *J* = 7.5 Hz), 7.58 (t, 2H, *J* = 5.1 Hz), 5.66 (m, 2H), 3.55 (br m, 2H), 3.42 (br m, 1H), 1.79 (m, 2H), 0.79 (t, 3H, *J* = 7.8 Hz); ^{19}F NMR (CD$_2$Cl$_2$) δ −79.1 (s, $CF_3SO_3^-$); ^{13}C NMR (CD$_2$Cl$_2$) δ 136.6, 134.1, 133.2, 132.6, 130.8, 129.7, 125.7, 123.4, ($CF_3SO_3^-$ not observed), 112.8, 43.0, 37.0, 27.7, 9.3; IR (CCl$_4$) 2973, 2969, 2935, 2878, 2263, 1559, 1540, 1471, 1444, 1244, 1027 cm^{-1}; FAB HRMS *m*/*z* calcd for $C_{15}H_{15}NI$ (M − $CF_3SO_4^-$) 336.02480, found 336.02378.

Acknowledgment. Financial support by the NCI and NIH 2R01CA16903 is gratefully acknowledged.

JO970651M