contribute to the rekindling of interest in this general area.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Varian EM-360L (60-MHz) NMR spectrometer with tetramethylsilane as internal standard. IR spectra were recorded on a Beckman IR-8 spectrometer. Mass spectra were obtained at 70 eV on a CEC-21-110B mass spectrometer and GC-MS with a Finnigan Model 4000 mass spectrometer, equipped with an Incos data system. Capillary GC analysis was performed with a Hewlett Packard Model 5790 gas chromatograph equipped with a flame ionization detector and a J&W DB-5 fused silica gel column (30 M × 0.255 mm i.d.; 0.25 μM film thickness). All the analyses were performed with a flow rate of 1 mL/min and with oven, injector, and detector temperatures of 90 °C, 250 °C, and 300 °C, respectively. Integrations and retention times were obtained with a Hewlett Packard Model 3390A integrator. Retention times (min) for compounds **1**, **2**, **3**, **6**, *p*-xylene, and undecane were found to be 11.7, 16.3/16.8, 11.4, 14.0, 3.5, and 9.3, respectively. Preparative GC was performed with a Varian Model 1520 gas chromatograph equipped with a thermal conductivity detector and a 10 ft 3 in. × $^3/_8$ in. column of Carbowax 20M on 80/100-mesh Chromosorb W-NAW. Helium was used as the carrier gas and liquid N_2 was used to condense the samples in collectors protected from moisture with $CaSO_4$. Rotating disk chromatography was performed with a Harrison Research Model 7924T "Chromatotron" using a 1-mm rotor coated with silica gel 60, PF-254 (EM Reagents 7749), and containing 3.85% silver nitrate. The coating of the rotor with silica gel/$AgNO_3$ followed the recipe provided by Harrison Research.

All glassware was cleaned in a KOH/2-propanol bath and then rinsed with dilute acetic acid followed by dilute ammonium hydroxide and finally distilled water before drying in an oven. Methanol (EM Science Omnisolv) was distilled from magnesium methoxide immediately prior to use. Microanalyses were performed by R. Wielesek at the University of Oregon, Eugene, OR.

Preparation of Samples of Syn Allene 1 and Anti Allene 3 for Photolysis. A mixture of **1** and **3** was prepared according to the method previously described.[1] Approximately 30 μL of a 40:60 mixture of **1** and **3** in 300 μL of hexane was applied to a silica gel/$AgNO_3$ rotor of a rotating disk chromatograph and first eluted with 75 mL of hexane. Elution was completed with three 75-mL portions of hexane containing 5%, 10%, and finally 20% by volume of ethyl acetate. In all, 75, 4-mL fractions were collected. Anti allene **3** was found to elute in fractions 31–38 and syn allene **1** in fractions 44–52 by capillary GC analysis. Solutions of **1** and **3** were concentrated below a Vigreux column with gentle heating and then solvent-free samples were obtained from the concentrated solutions by preparative GC (flow rate 40 mL/min, oven temperature 150 °C, injector temperature 150 °C, detector temperature 175 °C, retention time 24 min).

Preparation of a Sample of Trienes 2 for Photolysis. The sample was obtained from the thermal rearrangement of allene **1** on the preparative GC. Three injections of 10 to 15 μL each of a 46:54 mixture of **1** and **3** were made (flow rate 15 mL/min, oven temperature 220 °C, injector temperature 300 °C, detector temperature 230 °C). Approximately 12 mg of a 48:52 mixture of the diastereomers of **2** (retention time 31.5 min) and 20 mg of residual anti allene **3** (retention time 20.3 min) were obtained.

Photolyses of *syn*- and *anti*-7-(1,2-Butadienyl)bicyclo[2.2.1]hept-2-ene (1 and 3) [cf. Figure 1]. A 5.2-mg (35.6 μmol) sample of **1** or **3** was combined with 3.9 mg (36.7 μmol) of *p*-xylene (MCB) and 5.6 mg (35.8 μmol) of undecane (internal standard) in 5 mL of dry methanol in a 13 × 100 mm quartz tube. The tubes were sealed with septa and N_2 was bubbled through the solutions for 15 min immediately prior to irradiation.

The samples were irradiated for up to 50 h at a distance of 6 cm by using a Vicor-filtered Hanovia 450-W medium-pressure mercury arc lamp in a carrousel reaction apparatus. The course of the reactions was followed by monitoring the integrated intensity of the starting materials and products vs undecane on the capillary GC. Allene **1** was found to give *E* and *Z* trienes **2** as the only nonpolymeric product, whereas allene **3** gave only the reduced product **6**. A response ratio of 0.84 was determined for the 1/3 mixture vs undecane and used to correct the integrals for **1**, **3**, and **6**. Similarly, a response ratio of 1.3, determined for the mixture of both diastereomers of **2**, was used to correct the integrals for each separate diastereomer. The results are plotted in Figure 1.

Photolysis of a Mixture of (*E*)- and (*Z*)-1-Ethylidene-3a,4,5,7a-tetrahydroindene (2). This photolysis was carried out in the manner described above on a 20.0-mg (66 μmol) sample of a 48:52 mixture of the two diastereomers of **2**, using an equivalent each of *p*-xylene and undecane. Capillary GC analysis of the reaction mixture monitored over time revealed that one of the trienes first isomerized to the other before both of them completely polymerized over the course of a 28-h period.

Preparation of 7-(1,2-Butadienyl)bicyclo[2.2.1]heptane (6). The general procedure[1] used to prepare a mixture of **1** and **3** was followed with a substitution of 7-bromonorbornane[13] (1.5 g) for the *syn*-7-bromonorbornene: IR (neat) 2960, 2920, 2880, 1980 (C=C=C), 1480, 1460, 1440, 1375, 1350, 1310, 1275, 1255, 1210, 1185, 1135, 1075, 980, 870, 830, 775, 705, 675 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.9–2.1 (m, 11 H), 1.6 (dd, 3 H), 4.8–5.1 (m, 2 H); MS (EI), *m/z* (rel intensity) 148 (M^+, 13), 133 (10), 120 (15), 119 (27), 105 (45), 94 (88), 91 (85), 80 (100), 79 (100), 77 (40), 67 (30); high resolution MS (EI), *m/z* (M^+) calcd 148.125, obsd 148.125. Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.83; H, 11.17. The photoreduction product **6** obtained from **3** had the same retention time (14.0 min) on the capillary GC (co-injection) and gave an identical mass spectrum as the product prepared above.

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(13) Kwart, H.; Kaplan, L. *J. Am. Chem. Soc.* **1954**, *76*, 4072–4077.

Addition of *tert*-Butyl Hypoiodite to Selected Olefins

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In a continuation of our investigation of the electrophilic additions of alkyl hypohalites[1,2] to olefins, we report on

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(1) For previous studies on the addition of alkyl hypochlorites to olefins and dienes, see: (a) Heasley, G. E.; McCully, V. M.; Wiegman, R. T.; Heasley, V. L.; Skidgel, R. A. *J. Org. Chem.* **1976**, *41*, 644. (b) Heasley, G. E.; Emery, W. E. III; Hinton, R.; Shellhamer, D. F.; Heasley, V. L.; Rodgers, S. L. *Ibid.* **1978**, *43*, 361. (c) Heasley, V. L.; Shellhamer, D. F.; Gipe, R. K.; Wiese, H. C.; Oakes, M. L.; Heasley, G. E. *Tetrahedron Lett.* **1980**, *21*, 4133. (d) Heasley, V. L.; Gipe, R. K.; Martin, J. L.; Wiese, H. C.; Oakes, M. L.; Shellhamer, D. F.; Heasley, G. E.; Robinson, B. L. *J. Org. Chem.* **1983**, *48*, 3195 and other references included therein.

the addition of *tert*-butyl hypoiodite ($(CH_3)_3COI$, 1) to selected olefins. At the start of this study, we suspected that 1 might be sufficiently reactive to proceed ionically without the assistance of a catalyst such as boron trifluoride, BF_3, which was required for an ionic addition of the alkyl hypochlorites and hypobromites.[1c,d] If BF_3 catalyst was required, however, we were interested in observing whether fluoro iodides would be formed from 1 and olefins as was the case with the hypochlorites and hypobromites where fluoro chlorides and fluoro bromides were major products.[1d] Another point of interest was to determine whether 1 could be caused to react with styrene by a radical pathway as had been observed earlier for *tert*-butyl hypochlorite and *tert*-butyl hypobromite.[3]

A previous study[4,5] on the addition of 1 to olefins has been reported, but this study did not take into account the instability and moisture sensitivity of 1 or distinguish between ionic and radical additions. Furthermore, the stereochemistry and regiochemistry of the addition of 1 to olefins were not investigated.

Results and Discussion

Data from the addition of *tert*-butyl hypoiodite (1) to selected olefins are shown in Table I and in the Experimental Section. We observed that 1 and styrene in the dark reacted slowly to give the anti-Markovnikov regioisomer, 2-*tert*-butoxy-1-phenylethyl iodide. When the solution was irradiated with ultraviolet light, the anti-Markovnikov regioisomer was formed rapidly in high yield. We assume that these reactions are occurring by a radical mechanism. In the absence of light, the mechanism involves either thermal or molecule-induced radical formation. The Markovnikov regioisomer, 2-*tert*-butoxy-2-phenylethyl iodide, was produced in a rapid reaction when a few drops of BF_3 etherate were added to a mixture of styrene and 1. As the data in Table I show, BF_3 functions as a catalyst with all of the olefins. In some cases, the olefins and 1 react without BF_3: the β-methylstyrenes, slowly and good yield; the 4-octenes and *tert*-butyl ethylene, slowly and poor yield; styrene and 1-hexene, no reaction. Radical additions were not investigated with the other olefins except we observed qualitatively from MS analysis that the β-methylstyrenes and 1 in the presence of ultraviolet light did give the anti-Markovnikov regioisomer in low yield.

The function of BF_3 in the ionic reactions is probably the same as reported earlier for *tert*-butyl hypochlorite[1c,d] and *tert*-butyl hypobromite[1d] where it was postulated that BF_3 attacks the oxygen forming an ion pair (see below).


$$C_6H_5\overset{\overset{I}{/+\backslash}}{CHCH_2},\ BF_3OC(CH_3)_3^-$$

Apparently fluoride is not nucleophilic in this ion pair since no fluoro iodides were observed. *tert*-Butyl hypochlorite[1c,d] and *tert*-butyl hypobromite[1d] with styrene and BF_3 gave fluoro chloride and fluoro bromide products, respectively. The iodonium ion may be less reactive and more selective than the other halonium ions.

Ionic addition of 1 to the isomeric β-methylstyrenes is stereospecific as shown in Table I. Comparisons with data from the literature indicate that the additions occur with anti orientation. This conclusion is based on the relative chemical shifts of the β-methyl protons in the *tert*-butoxy iodides and on comparisons with additions of several iodine electrophiles to various olefins. Rolston and Yates[6] have shown that the chemical shift (ppm) of the β-methyl proton is consistently higher for the erythro stereoisomer than the threo stereoisomer, as shown in the following adducts for the β-methylstyrenes, respectively: dichloride, 1.68 and 1.41; dibromide, 2.00 and 1.60; acetoxy bromides, 1.55 and 1.45. The chemical shifts of the β-methyl protons from the *tert*-butoxy iodides from (*E*)-β-methylstyrene and (*Z*)-β-methylstyrene are 1.78 and 1.68, respectively, indicating that the former stereoisomer is erythro and the latter threo. Furthermore, only anti addition has been reported with other iodine electrophiles: iodine azide[7] to cyclohexene, 2-cholestene, the isomeric butenes, and the isomeric stilbenes; iodine isocyanate[8,9] to (*Z*)-β-deuteriostyrene; iodonium nitrate[10] to (*Z*)-β-deuteriostyrene and the isomeric stilbenes.

Stereospecific additions of 1 to the β-methylstyrenes are in contrast with *tert*-butyl hypochlorite and *tert*-butyl hypobromite, which add nonstereospecifically with the same olefins. Apparently, the bridging in the intermediate chloronium ion and bromonium ion is not as symmetrical as in the iodonium ion. Consequently, charge develops on the benzylic carbon, and rotation occurs around the carbon–carbon bond leading to a mixture of diastereomers.

The data in Table I indicate that addition of 1 to the isomeric 4-octenes is also stereospecific. We are suggesting that this addition occurs by anti orientation by analogy with the β-methylstyrenes and the other iodine electrophile–olefin systems.

tert-Butylethylene and 1 reacted to give only the anti-Markovnikov regioisomer, as shown in Table I. These results parallel those from iodonium nitrate,[11] bromonium nitrate,[12] iodine isocyanate,[9] iodine azide,[7] and Br_2 in methanol[13] where only the anti-Markovnikov regioisomers were observed in additions to *tert*-butylethylene. Absence of product derived from rearrangement of the methyl group, which was observed in the additions of HCl,[14] Cl_2,[15] and Br_2[16] to *tert*-butylethylene, indicates that bridging is symmetrical in the intermediate iodonium ion from *tert*-butylethylene and 1.

The data in Table I show that 1 adds to 1-hexene to give both Markovnikov and anti-Markovnikov *tert*-butoxy-

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(2) For previous studies on the addition of alkyl hypobromites to olefins and dienes, see: (a) Heasley, V. L.; Frye, C. L.; Heasley, G. E.; Martin, K. A.; Redfield, D. A.; Wilday, P. S. *Tetrahedron Lett.* **1970**, 1573. (b) Heasley, V. L.; Titterington, D. R.; Rold, T. L.; Heasley, G. E. *J. Org. Chem.* **1976**, *41*, 1285. (c) Reference 1d and other references included therein.

(3) Walling, C.; Heaton, L.; Tanner, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 1715.

(4) Glover, S. A.; Goosen, A. *Tetrahedron Lett.* **1980**, *21*, 2005.

(5) Glover and Goosen[4] carried out the reactions in refluxing *tert*-butyl alcohol (except for one reaction in refluxing benzene), without protection from moisture during synthesis or reaction, and at a 5:1 ratio of 1/olefins. BF_3 was not used to catalyze an ionic reaction. We repeated one of the reactions described by Glover and Gossen[4] by adding 1, prepared by their procedure and by ours, and obtained only 2-*tert*-butoxy-1-phenylethyl iodide (anti-Markovnikov), not 2-*tert*-butoxy-2-phenylethyl iodide (Markovnikov) as they described.

(6) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469.

(7) Fowler, F. W.; Hassner, A.; Levy, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 2077.

(8) Hassner, A.; Heathcock, C. C. *Tetrahedron Lett.* **1964**, 1125.

(9) Hassner, A.; Hoblitt, R. P.; Heathcock, C.; Kropp, J. E.; Lorber, M. *J. Am. Chem. Soc.* **1970**, *92*, 1326.

(10) Lown, J. W.; Joshua, A. V. *J. Chem. Soc., Perkin Trans 1* **1973**, 2680.

(11) Diner, U. E.; Lown, J. W. *J. Chem. Soc. 1* **1970**, *333*.

(12) Lown, J. W.; Joshua, A. V. *Can. J. Chem.* **1977**, *55*, 508.

(13) Puterbaugh, W. H.; Newman, M. S. *J. Am. Chem. Soc.* **1957**, *79*, 3469.

(14) Fahey, R. C.; McPherson, C. A. *J. Am. Chem. Soc.* **1969**, *91*, 3865.

(15) Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 4285.

(16) Rearrangement is a major product during bromination at room temperature, but does not occur at –78 °C: Collier, W. L.; Macomber, R. S. *J. Org. Chem.* **1973**, *38*, 1367.

iodohexane regioisomers, with the latter in predominance. This result is in contrast to other electrophilic additions to 1-hexene in which the Markovnikov regioisomer is formed in greater amount. A radical addition is not involved since the ratio of regioisomers remained the same in the dark and in the presence of the radical inhibitor oxygen. Ratios of Markovnikov to anti-Markovnikov regioisomers for various electrophiles are as follows: iodinium nitrate,[10] 100:0; iodine isocyanate,[9] 70:30; iodine azide,[7] 100:0; iodine chloride, 57:40;[17] bromonium nitrate, ca. 60:40;[12] and methyl hypobromite, 71:29.[2a] Formation of more anti-Markovnikov regioisomer in the case of 1 is probably due to greater steric hindrance as the bulky *tert*-butoxide ion attacks the intermediate iodonium ion.

Experimental Section

General Procedures. All reagents, except the β-methylstyrenes, were distilled prior to use. CCl_4 was distilled from the stored over P_2O_5. CCl_4 was also adequately dried by storage over molecular sieves. NMR spectra were obtained on a Varian T60A spectrophotometer and on a 500-MHz instrument located at the National Science Foundation Regional Center at California Institute of Technology in Pasadena, CA. Me_4Si was employed as the reference standard. Mass spectral analyses were obtained at 70 eV on a Hewlett-Packard 5790 A GC interfaced with an HP 5970 A mass selective detector.

Elemental analyses were not obtained because of the instability of the *tert*-butoxy iodides. All structures are based on NMR and/or MS analyses.

Preparation and Use of *tert*-Butyl Hypoiodide (1). *tert*-Butyl hypoiodite (1) was prepared according to the procedures ($(CH_3)_3COCl + HgCl_2$ and $(CH_3)_3COK + I_2$) of Tanner et al.[18] Although not emphasized previously,[4,17] we found that 1 was sensitive to moisture. For example, when 1 was placed on a watchglass in the laboratory, it was rapidly converted to I_2 (1–2 min). Consequently, preparation and reactions were carried out in a dry box in dry N_2 and exposed P_2O_5. The reactivity of 1 with H_2O is in contrast to $(CH_3)_3COCl$ and $(CH_3)_3COBr$, which can be prepared and isolated over H_2O.

The yield of 1 from $(CH_3)_3COCl$, based on iodometric titration, was approximately 90%. This included approximately 10% I_2 as reported by Tanner et al.[18] We were unable to determine the amount of I_2 in the preparation of 1 by UV–vis spectroscopy because of the rapid decomposition of 1 to I_2 in the cell. A peak at 402 nm was initially observed, which rapidly disappeared with a concomitant increase in the peak at 506 (I_2). We estimated that the concentration of 1 was 80–85% on the basis of iodometric titrations and the presence of I_2 (10%).

Reaction Conditions. Reactions with 1 were either carried out in a drybox or in a flask equipped with a rubber septum through which the reactant (1) could be added with a syringe. Sufficient 1 was added to a stirred solution (0.02 mol fraction in olefin) to react with ca. 80% of the olefin. A few drops of BF_3 (boron trifluoride etherate) were added to the reaction mixture. The color changed immediately from the orange-red of 1 to the slight purple of unreacted iodine. Water was then added to destroy the BF_3, the organic layer was isolated and dried, and the solution was analyzed. The radical addition of 1 to styrene was carried out by irradiating a solution of styrene (mol fraction of 0.8) in CCl_4 with a sunlamp until a color change occurred.

All of the products except those from *tert*-butyl hypobromite were isolated in approximately 25% yield by column chromatography on silica gel with petroleum ether and increasing amounts of ether. Attempts at further purification by distillation failed because of decomposition.

Reaction with Styrene. 2-*tert*-Butoxy-2-phenylethyl iodide ($C_6H_5CHOC(CH_3)_3CH_2I$): NMR (500 MHz, CCl_4) δ 1.09 (s, 9 H), 3.14 (d, J = 6.4 Hz, 2 H), 4.98 (t, J = 6.4 Hz, 1 H), 7.27–7.16 (m, 5 H); mass spectrum, m/e (relative intensity) M – I 177 (0.07), M – CH_2I 163 (87), C_6H_5CHOH 107 (100), C_6H_5CO 105 (16), 104 (96), 103 (29), C_4H_9 57 (100).

2-*tert*-Butoxy-1-phenylethyl iodide ($C_6H_5CHICH_2OC(CH_3)_3$): NMR (500 MHz, CCl_4) δ 1.10 (s, 9 H), 3.62 (dd, J = 7.2 and J = 9.8 Hz, 1 H), 3.79 (dd, J = 7.2 and 9.8 Hz, 1 H), 5.00 (dd, J = 7.2 and 7.2 Hz, 1 H), 7.31–7.14 (m, 5 H); mass spectrum, m/e M – I 177 (1), C_6H_5CO 105 (3), 104 (3), 103 (2), C_4H_9 57 (100).

The two regioisomers were separated on a 6 ft × 0.25 in. 2.5% SE-30 glass column (column A) at 140 °C with the following retention times (min): M, 6.4 and AM, 7.3. Retention times on a 25-m, methyl silicone capillary column (column B), programed from 130–190 °C, 15 °C/min, were (min) M, 9.3 and AM, 11.1.

Reaction with (*E*)- and (*Z*)-β-Methylstyrene. *erythro*-1-*tert*-Butoxy-1-phenyl-2-iodopropane ($C_6H_5CHOC(CH_3)_3CHICH_3$) from (*E*)-β-methylstyrene: NMR (500 MHz, CCl_4) δ 1.14 (s, 9 H), 1.78 (d, J = 7.0 Hz, 3 H), 4.15–4.17 (m, 1 H), 4.62 (d, J = 4.9 Hz, 1 H), 7.2–7.33 (m, 5 H).

***threo*-1-*tert*-Butoxy-1-phenyl-2-iodopropane** ($C_6H_5CHOC(CH_3)_3CHICH_3$) from (*Z*)-β-methylstyrene: NMR (500 MHz, CCl_4) δ 1.13 (s, 9 H), 1.68 (d, J = 7.0 Hz, 3 H), 4.14 (quintet, J = 7.0 and J = 6.8 Hz, 1 H), 4.36 (d, J = 6.8 Hz, 1 H), 7.24–7.34 (m, 5 H).

Mass spectra (identical) for the two diastereomers: M – C_4H_9O, 245 (3); M – I, 191 (0.3), M – $CHICH_3$, 163 (4); 135 (11); 118 (26); 117 (22), C_6H_5CHOH, 107 (84); C_7H_7, 91 (12); C_4H_9, 57 (100).

The diasteromers had identical retention times on column A or B. They were isolated by column chromatography from the appropriate β-methylstyrene, and their structures were established by their NMR and mass spectra. The stereospecificities of the additions are based on the fact that NMR spectra of the isolated products indicated a different diastereomer for each olefin.

Reaction with (*E*)- and (*Z*)-4-Octene. *erythro*-4-*tert*-Butoxy-5-iodooctane ($C_3H_7CHOC(CH_3)_3CHIC_3H_7$) from (*E*)-4-octene: NMR (60 MHz, CCl_4) δ 0.70–2.42 (m, 23 H), 2.76–3.16 (m, 1 H), 3.96–4.38 (m, 1 H).

***threo*-4-*tert*-Butoxy-5-iodooctane** ($C_3H_7CHOC(CH_3)_3CHIC_3H_7$) from (*Z*)-4-octene: NMR (60 Hz, CCl_4) δ 0.77–2.28 (m, 23 H), 3.47–3.84 (m, 1 H), 3.90–4.30 (m, 1 H).

Mass spectrum (identical) for the two diastereomers: M – I, 185 (1); $C_3H_7CH(O)C_4H_9$, 129 (32); 111 (4); $C_3H_7CH(O)H$, 73 (7); C_5H_9, 69 (20); $(CH_3)_3C$, 57 (100); C_4H_7, 55 (24); C_3H_5, 41 (39).

The diastereomers were separated on column A (min) at 135 °C: erythro, 5.3 and threo, 4.8. The retention times (min) on column B, programmed from 120–180 °C, 15 °C/min, were erythro, 8.7 and threo, 8.1.

Reaction with *tert*-Butylethylene. 1-*tert*-Butoxy-2-iodo-3,3-dimethylbutane ($(CH_3)_3CCHICH_2OC(CH_3)_3$): NMR (60 MHz, CCl_4) δ 1.09 (s, 9 H), 1.06 (s, 9 H), 3.46–4.24 (m, 3 H). Another small singlet was observed at 1.07 ppm, which probably arises from conformers due to slow rotation because of the large *tert*-butyl groups and the iodine.

Mass spectrum: M, 284 (0.2); 157 (2); $C_6H_{13}O$, 101 (8); $(CH_3)_3C(O)CH_2$, 87 (6); $(CH_3)_3C$, 57 (100); C_2H_3O, 43 (8).

Absence of the Markovnikov regioisomer is based on the fact that no mass at m/z 143 (M – CH_2I or $C_4H_9CH(O)C_4H_9$) was observed. This is a prominent peak in the mass spectra of all of the other terminal iodides. Furthremore, only one peak was observed under all GC analysis conditions: column A (min) at 106 °C, 6.5; column B (min) programmed from 100–190 °C, 10 °C/min, 18. Rearrangement is doubtful since the most likely products, $(CH_3)_2CICH(CH_3)CH_2OC(CH_3)_3$ and/or $CH_2{=}C(CH_3)CH(CH_3)CH_2OC(CH_3)_3$, were not observed.

Reaction with 1-Hexene. 1-*tert*-Butoxy-2-iodohexane $CH_3(CH_2)_3CHICH_2OC(CH_3)_3$: mass spectrum, m/e M 284 (.07), M – I 157 (2), 83 (18), $(CH_3)_3C$ 57 (100).

2-*tert*-Butoxy-1-iodohexane $CH_3(CH_2)_3CHOC(CH_3)_3CH_2I$: mass spectrum, m/e M – $CH_3(CH_2)_3$ 221 (7), M – CH_2I 143 (16), 83 (12), $(CH_3)_3$ C 57 (100); NMR (mixture of regioisomers, 60 MHz, CCl_4) δ 0.67–2.00 (m, 18 H), 2.89–3.76 (m, 3 H); GC analysis column A (min) at 105 °C 9.4, column B (min), programed from 100–190 °C, 1 °C/min M, 20.9 and AM, 21.3.

Reaction of *tert*-Butyl Hypochlorite ($(CH_3)_3COCl$) with (*E*)- and (*Z*)-β-Methylstyrene. The reactions were performed under the same conditions (ionic BF_3) as described for the β-methylstyrenes and 1. GC analysis (column B, programmed from 100–150 °C, 15 °C/min) gave two compounds with retention times

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(17) Unpublished data from our laboratory.

(18) Tanner, D. D.; Gidley, G. C.; Das, N.; Rowe, J. E.; Potter, A. *J. Am. Chem. Soc.* **1984**, *106*, 5261.

Table I. Addition of *tert*-Butyl Hypoiodite (1) to Selected Olefins in CCl_4

olefin	condition[a]	product	yield,[b] %
styrene	BF_3	2-*tert*-butoxy-2-phenylethyl iodide	95
styrene	UV	2-*tert*-butoxy-1-phenylethyl iodide	83
(*E*)-β-methylstyrene	BF_3	*erythro*-1-*tert*-butoxy-1-phenyl-2-iodopropane	100
(*Z*)-β-methylstyrene	BF_3	*threo*-1-*tert*-butoxy-1-phenyl-2-iodopropane	92
(*E*)-4-octene	BF_3	*erythro*-4-*tert*-butoxy-5-iodooctane	85
(*Z*)-4-octene	BF_3	*threo*-4-*tert*-butoxy-5-iodooctane	*c*
tert-butylethylene	BF_3	1-*tert*-butoxy-2-iodo-3,3-dimethylbutane	54
1-hexene	BF_3[f]	2-*tert*-butoxy-1-iodohexane (38%)[d] 1-*tert*-butoxy-2-iodohexane (62%)[e]	75

[a] All reactions were done in CCl_4 at room temperature. [b] Yields are based on GC analyses. [c] Yield was not determined. [d] Markovnikov regioisomer (M). [e] Anti-Markovnikov (AM) regioisomer. [f] The same ratio of products was obtained in the dark with O_2 present as a radical inhibitor.

(min) at 11.2 and 11.5. (Fluoro chlorides were also observed). The GC analyses from either (*E*)- or (*Z*)-β-methylstyrene and *tert*-butyl hypochlorite were identical. The diastereomers were present in nearly equal amounts. The mass spectra were identical, indicating that they were a mixture of diastereomers, *erythro*- and *threo*-1-*tert*-butoxy-1-phenyl-2-chloropropane. The mass spectra confirmed these structures. Mass spectrum, *m/e* M − CH_2Cl 163 (19), M − C_4H_9O (chlorine isotopes) 155 (2) and 153 (7), 117 (9), 115 (9), C_6H_5CHOH 107 (100), C_6H_5CO 105 (7), C_7H_7 91 (10), 79 (15), C_4H_9 57 (54).

Reaction of *tert*-Butyl Hypobromite ($(CH_3)_3COBr$) with (*Z*)-β-Methylstyrene. *tert*-Butyl hypobromite was added to (*Z*)-β-methylstyrene under the same conditions as for 1 and *tert*-butyl hypochlorite. GC analysis (column B, programmed from 120–170 °C, 15 °C/min) showed two diastereomers with retention times (min) of 10.6 and 10.8 in a 3:1 ratio, respectively. (Fluoro bromides were also observed.) The mass spectra were identical and, on the basis of the spectra, were assigned as a mixture (diastereomers) of *erythro*- and *threo*-1-*tert*-butoxy-1-phenyl-2-bromopropane: mass spectrum, *m/e* M − C_4H_9O (bromine isotopes) 199 (8) and 197 (8), $C_6H_5CH(O)C_4H_9$ 163 (25), 117 (16), 115 (7), C_6H_5CHOH 107 (100), C_6H_5CO 105 (8), C_7H_7 91 (10), 79 (14), C_4H_9 57 (52).

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Registry No. 1, 917-97-5; PhCH=CH_2, 100-42-5; (*E*)-PhCH=CHMe, 873-66-5; (*Z*)-PhCH=CHMe, 766-90-5; (*E*)-PrCH=CHPr, 14850-23-8; (*Z*)-PrCH=CHPr, 7642-15-1; CH_2=CHBu-*t*, 558-37-2; CH_2=CHBu, 592-41-6; PhCH(OBu-*t*)CH_2I, 13684-99-6; PhCHICH_2OBu-*t*, 111558-77-1; *erythro*-PhCH(OBu-*t*)CHIMe, 111558-78-2; *threo*-PhCH(OBu-*t*)CHIMe, 111558-79-3; *erythro*-PrCH(OBu-*t*)CHIPr, 111558-80-6; *trheo*-PrCH(OBu-*t*)CHIPr, 111558-81-7; *t*-BuOCH_2CHIBu-*t*, 111558-82-8; BuCH(OBu-*t*)CH_2I, 111558-83-9; *t*-BuOCH_2CHIBu, 111558-84-0; *erythro*-PhCH(OBu-*t*)CHClMe, 111558-85-1; ClO-Bu-*t*, 507-40-4; *threo*-PhCH(OBu-*t*)CHClMe, 111558-86-2; BrO-Bu-*t*, 1611-82-1; *erythro*-PhCH(OBu-*t*)CHBrMe, 111558-87-3; *threo*-PhCH(OBu-*t*)CHBrMe, 111558-88-4.

Synthesis of 4,5:4′,5′-Bis(propylene-1,3-diseleno)tetrathiafulvalene

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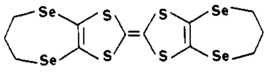
Because of the unique transport properties of charge-transfer (C-T) complexes based on the π-electron-donor molecules, 4,5:4′,5′-bis(alkylenedithio)tetrathiafulvalenes,[1] the properties of the partially selenium substituted donor 4,5:4′,5′-bis(propylene-1,3-diseleno)tetrathiafulvalene (BPDSe-TTF, 1)[2] were investigated. This molecule was



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of particular interest to us since much of the current research in this area[3] has focused on increasing the dimensionality of the transport in C-T salts derived from these donors. One of the simplest ways of increasing dimensionality[4,5] is to incorporate either selenium or tellurium into the donor molecules.[6,7] The increased overlap expected from the larger orbitals of these chalcogens is believed to increase both inter- and intramolecular overlaps, thereby enhancing conductivity in at least two directions, and thus impart greater two-dimensional character to their C-T salts. In addition, the greater steric requirements of the bulky diselenopropylene groups of 1 are expected to lead to an expansion of the unit cell and thereby favorably affect electronic properties. In this paper, I report the synthesis of BPDSe-TTF and describe some selected physical properties of this donor.

Results and Discussion

Several chalcogen-substituted TTFs have been reported in the literature. The first reported procedure for incorporating four tellurium atoms onto the TTF skeleton involves lithiation of TTF followed by reaction with elemental tellurium to give a TTF tetratelluride anion.[6] Attempts to cap this anion with dihaloalkanes resulted in the formation of uncharacterized solids. These results suggest that in the tellurium-substituted system only tetrakis(alkyltelluro)-TTF is isolable since insertion of methylene or ethylene groups might be difficult for steric reasons. More recently, the synthesis of the methylenediseleno-substituted TTF, BMDSe-TTF, and the ethylenediseleno-substituted TTF, BEDSe-TTF, has been reported by Lee,[7] who used a similar procedure to that described above for tellurium insertion. These partially selenium substituted donors were prepared by blocking the

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(1) (a) Nigrey, P. J.; Morosin, B.; Kwak, J. F.; Venturini, E. L.; Baughman, R. J. *Synth. Met.* **1986**, 15. (b) Nigrey, P. J.; Morosin, B.; Venturini, E. L.; Azevedo, L. J.; Schirber, J. E.; Perschke, S. E.; Williams, J. E. *Physica B* **1986**, *143B*, 290.

(2) Recommended IUPAC name: 6,6′,7,7′-tetrahydro-$\Delta^{2,2'}$-bi-5*H*-[1,4]diselenepino[2,3-*d*]-1,3-dithiole. Current *Chemical Abstracts* name: 2-(6,7-dihydro-5*H*-[1,4]diselenepino[2,3-*d*]-1,3-dithiol-2-ylidene)-6,7-dihydro-5*H*-[1,4]diselenepino[2,3-*d*]-1,3-dithiole.

(3) For some recent reviews, see: Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Emge, T. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1985**, *18*, 261 and the Proceedings of the National Conference on Science and Technology of Synthetic Metals, Kyoto, Japan, June 1–6 (*Synth. Met.* **1987**, *19*).

(4) Bechgaard, K.; Cowan, D. O.; Bloch, A. N. *J. Chem. Soc., Chem. Commun.* **1974**, 937.

(5) Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1984**, *106*, 8303.

(6) Aharon-Shalmon, E.; Becker, J. Y.; Bernstein, J.; Bittner, S.; Shaik, S. *Tetrahedron Lett.* **1985**, *26*, 2783.

(7) Lee, V. Y. *Synth. Met.* **1987**, *20*, 161.

0022-3263/88/1953-0201$01.50/0