eluting solvent: UV (MeOH) 218 nm, 266, 277, 289 (ε 37 500, 77 900, 65 600, 44 100); NMR ($CDCl_3$) δ 0.03 (s, 9 H, Me_3Si), 0.90 (t, 2 H, J = 8 Hz, CH_2Si), 3.65 (t, 2 H, J = 8 Hz, OCH_2), 5.65 (s, 2 H, NCH_2O), 6.65 (d, 1 H, J = 3 Hz, H-3), 7.35 (m, 3 H), 7.65 (m, 2 H). Anal. Calcd for $C_{14}H_{21}NOSi$: C, 67.96; H, 8.56; N, 5.66. Found: C, 67.82; H, 8.39; N, 5.73.

Deprotection of Pyrroles and Indole. Method Ia. Pyrrole-2-carboxaldehyde. To a stirred solution of the silyl compound **3b** (1.00 g, 4.4 mmol) in dichloromethane (132 mL) cooled to 0 °C was added slowly boron trifluoride etherate (2.1 mL, 17.8 mmol). The solution was left to come to room temperature after which time stirring was continued for 1 h. Sodium bicarbonate solution (10%, 20 mL) was added, and the organic phase was separated and evaporated in vacuo. Acetonitrile (132 mL) and Triton B (40% in methanol, 20 drops) were added, and the solution was stirred at reflux temperature for 6.5 h. The solution was poured into water and extracted with ether. The extract was washed with water, dried over magnesium sulfate, and evaporated in vacuo. The crude product was subjected to column chromatography on silica gel with hexane–ethyl acetate (80:20) as the eluting solvent to give pyrrole-2-carboxaldehyde: 0.360 g (86%); mp 43 °C.

2-Acetylpyrrole. The procedure for method Ia was followed except that the reaction with boron trifluoride etherate was carried out for only 0.5 h at room temperature, and the reflux period with Triton B was shortened to 3 h.

Method Ib. 2-Benzoylpyrrole. The procedure described in Ia was followed except that 5 equiv of boron trifluoride etherate was used, and the reaction mixture was stirred at room temperature for 0.25 h. The dichloromethane was not removed; instead, aqueous sodium acetate (10 equiv of a 5.5 M solution) was added, and the mixture was heated at reflux temperature for 1 h. The organic phase was separated, dried, and then worked up as described above.

Method II. Indole. A mixture of 1-[[2-(trimethylsilyl)ethoxy]methyl]indole (0.50 g, 2.0 mmol), tetra-*n*-butylammonium fluoride (1.59 g, 6.1 mmol), DMF (2.2 mL), and ethylenediamine (0.8 mL) was stirred at 45 °C for 48 h. The reaction mixture was poured into water and extracted with ether. The extract was washed successively with dilute hydrochloric acid and 10% sodium bicarbonate solution, and after the extract was dried, the ether was removed in vacuo. The residue was subjected to column chromatography on silica gel with hexane–ethyl acetate (4:1) as the eluting solvent. Indole (mp 50 °C) was thus obtained in 98% yield.

2-Benzylpyrrole (1e). 1-[[2-(Trimethylsilyl)ethoxy]methyl]-2-benzylpyrrole (**3g**) was deblocked in a manner identical with that described for **6**. The chromatographically homogeneous oil, obtained in 67% yield, contained less than 7% 2,5-dibenzylpyrrole by mass spectral analysis while the IR and NMR spectral properties were identical with those of authentic 2-benzylpyrrole.[16]

Lithiation and Alkylation of 1-[[2-(Trimethylsilyl)ethoxy]methyl]pyrrole. 1-[[2-(Trimethylsilyl)ethoxy]methyl]-2-methylpyrrole (3e) and 1-[[2-(Trimethylsilyl)ethoxy]methyl]-2,5-dimethylpyrrole (8a). To a solution of **3a** (0.20 g, 1.015 mmol) in dry hexane (1 mL) was added 2.1 M *tert*-butyllithium in hexane (0.48 mL, 1.008 mmol) at −10 °C. The solution was then left to stir at room temperature for 0.5 h, and then it was cooled to −78 °C whereupon a solution of methyl iodide (0.6 mL, 9.2 mmol) in anhydrous THF (1 mL) was added. Stirring was continued at −78 °C for 1 h, at 0 °C for 2 h, and at room temperature for 18 h. The solution was diluted with water and extracted with ether, and the extract was washed with saturated salt solution and dried. The solvent was removed in vacuo, and the residual oil (0.175 g) was shown by gas–liquid partition chromatography (3% SE-30, 100 °C) to consist of a 3:1 mixture of the 2-alkylated and 2,5-dialkylated pyrroles **3e** and **8a**: UV (MeOH) 214 nm (ε 6070); NMR ($CDCl_3$) δ 0.03 (s, 9 H, Me_3Si), 0.90 (t, 2 H, J = 8 Hz, CH_2Si), 2.20 (s, 3 H, CH_3), 3.60 (t, 2 H, J = 8 Hz, OCH_2), 5.30 (s, 2 H, N–CH_2O), 5.90 (m, 1 H, H-3), 6.15 (t, 1 H, H-4), 6.70 (dd, 1 H, $J_{4,5}$ = 3.0 Hz, $J_{3,5}$ = 1.8 Hz, H-5); MS, calcd for $C_{12}H_{23}NOSi$ (molecular ion) m/e 211.1392, found m/e 211.1394. The presence of the dimethyl compound **8a** in this mixture was supported by NMR resonances at δ 5.12 (s, N–CH_2O) and 5.79 (s, H-3,4) and a mass spectral molecular ion at m/e 225.

1-[[2-(Trimethylsilyl)ethoxy]methyl]-2-*n*-butylpyrrole (3f) and 1-[[2-(Trimethylsilyl)ethoxy]methyl]-2,5-di-*n*-butylpyrrole (8b). This mixture was obtained in exactly the same manner as described above. The components were separated by centrifugally accelerated TLC on silica gel using hexane–ethyl acetate (95:5) as the developing solvent. The mono-*n*-butyl compound **3f** was obtained as an oil: 43% yield; UV (MeOH) 218 nm (ε 6840); NMR ($CDCl_3$) δ 0.03 (s, 9 H, Me_3Si), 0.89 (t, 2 H, J = 8 Hz, CH_2Si), 0.95 (t, 3 H, J = 7 Hz, CH_3), 1.40 (m, 2 H, γ-CH_2), 1.65 (m, 2 H, β-CH_2), 2.60 (t, 2 H, J = 7 Hz, α-CH_2), 3.45 (t, 2 H, J = 8 Hz, OCH_2), 5.18 (s, 2 H, NCH_2O), 5.93 (M, 1 H, H-4), 6.09 (m, 1 H, H-3), 6.65 (m, 1 H, H-5). Anal. Calcd for $C_{14}H_{27}NOSi$: C, 66.34; H, 10.74; N, 5.53. Found: C, 66.48; H, 10.74; N, 5.50.

The 2,5-di-*n*-butyl compound **8b** was also obtained as an oil (22% yield); UV (MeOH) 225 nm (ε 6700); NMR ($CDCl_3$) δ 0.03 (s, 9 H, Me_3Si), 0.92 (t, 2 H, J = 8 Hz, CH_2Si), 0.95 (t, 6 H, J = 7 Hz, CH_3), 1.45 (m, 4 H, γ-CH_2), 1.65 (m, 4 H, β-CH_2), 2.60 (t, 2 H, J = 7 Hz, α-CH_2), 3.50 (t, 2 H, J = 8 Hz, OCH_2), 5.13 (s, 2 H, NCH_2O), 5.85 (s, 2 H, H-3,4). Anal. Calcd for $C_{18}H_{35}NOSi$; C, 69.85; H, 11.39; N, 4.53. Found: C, 70.16; H, 11.18; N, 4.28.

1-[[2-(Trimethylsilyl)ethoxy]methyl]-2-benzylpyrrole (3g). This compound was obtained as described above in 75% yield after purification by centrifugally accelerated TLC on silica gel. For analysis, a small quantity was distilled: bp 60–65 °C (0.015 mm); UV (MeOH) 205 nm, 269 (ε 13 700; 426); NMR ($CDCl_3$) δ 0.03 (s, 9 H, Me_3Si), 0.85 (t, 2 H, J = 8 Hz, CH_2Si), 3.40 (t, 2 H, J = 8 Hz, CH_2O), 4.05 (s, 2 H, CH_2), 5.10 (s, 2 H, NCH_2O), 5.95 (m, 1 H, H-4), 6.12 (m, 1 H, H-3), 6.73 (m, 1 H, H-5), 7.30 (m, 5 H, C_6H_5). Anal. Calcd for $C_{17}H_{25}NOSi$: C, 71.08; H, 8.71; N, 4.88. Found: C, 71.27; H, 8.90; N, 4.70.

Registry No. **1a**, 109-97-7; **1b**, 1003-29-8; **1c**, 1072-83-9; **1d**, 7697-46-3; **1e**, 33234-48-9; **2**, 76513-69-4; **3a**, 87954-20-9; **3b**, 87954-21-0; **3c**, 87954-22-1; **3d**, 87954-23-2; **3e**, 87954-24-3; **3f**, 87954-25-4; **3g**, 87954-26-5; **5**, 120-72-9; **6**, 87954-27-6; **8a**, 87954-28-7; **8b**, 87954-29-8.

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Difluorodiiodomethane: Its Preparation, Properties, and Free-Radical Reactions

Seth Elsheimer, William R. Dolbier, Jr.,* and Mark Murla

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Konrad Seppelt and Gerhard Paprott

Freie Universität Berlin Institut für Anorganische und Analytische Chemie, 1000 Berlin 33, West Germany

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Contrary to what its simple formula would suggest, CF_2I_2 has previously been available in only small amounts via difficult or low-yield procedures involving the addition of difluorocarbene to molecular iodine.[1] Clearly any routine use of CF_2I_2 requires a more practical source. We report the preparation of this potentially useful reagent in reasonable yields by fluorination of the readily available tetraiodomethane[2] with mercury(II) fluoride[3] (eq 1). The

$$CI_4 + HgF_2 \rightarrow CF_2I_2 + HgI_2 \quad (1)$$

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(3) An attempt to carry out this transformation by using a 9:1 molar ratio of KF/HgF gave unsatisfactory results.

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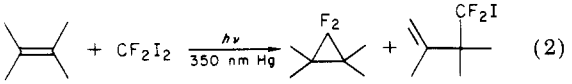
key to the success of this synthesis is the distillation of the product CF_2I_2 from the reaction mixture so as to minimize the extent of fluorination.

CF_2I_2 is a pale yellow liquid which at room temperature or upon exposure to light quickly acquires the characteristic burgundy color of I_2-containing solutions. Although refrigeration is recommended, only minor decomposition (<2%) is observed when CF_2I_2 is stored at room temperature in a Pyrex flask for several weeks. It is stable indefinitely at −78 °C.

Our interest in CF_2I_2 stems from its potential utility as a photochemical or organometallic source of difluorocarbene and its free-radical addition reactions with olefins.

Indeed, photolysis of CF_2I_2 in the presence of an excess of 2,3-dimethyl-2-butene, using Hg as an I_2 scavenger, led to a 25% yield of the expected carbene adduct **1**, along with 29% of **2** (eq 2), a product derived from free-radical



(2)

1 (25%) 2 (29%)

addition of $\cdot CF_2I$ to the alkene. This result can be compared with the photochemical cyclopropane-forming reactions of CH_2I_2[4] and $CHFI_2$.[5] Interestingly, while I_2 is obviously being generated reversibly in solutions of CF_2I_2 at room temperature, CF_2I_2 is not a *thermal* source of difluorocarbene inasmuch as the heating of it with 2,3-dimethyl-2-butene at 87 °C for 32 h led to a virtually complete recovery of starting materials. At the present time there is not indication that CF_2I_2 *will* provide a good synthetic source of difluorocarbene although work continues toward that goal, particularly with respect to its organometallic chemistry.

CF_2I_2, as expected, proved to be an excellent reagent for free-radical chain additions to alkenes. Its addition to 1-hexene and methyl propenoate for example proceeded smoothly in 73% and 47% isolated yields, respectively (eq 3 and 4). Such reactions of CF_2I_2 are much preferred over

$$CH_2{=}CH(CH_2)_3CH_3 + CF_2I_2 \xrightarrow[(BzO)_2]{\Delta} CF_2ICH_2CHI(CH_2)_3CH_3 \ (73\%) \quad (3)$$

3

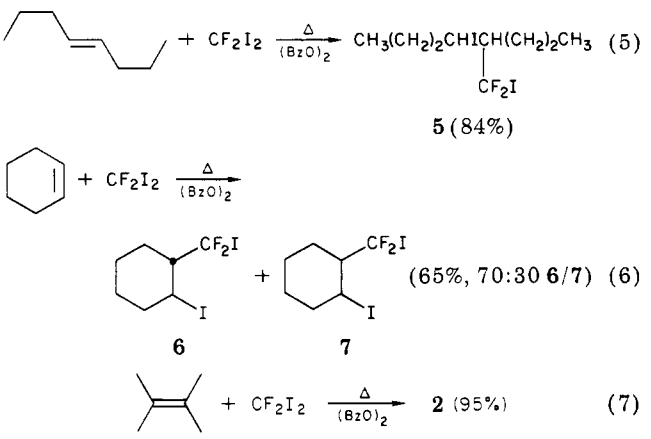
$$CH_2{=}CHCO_2CH_3 + CF_2I_2 \xrightarrow[(BzO)_2]{\Delta} CF_2ICH_2CHICO_2CH_3 \ (47\%) \quad (4)$$

4

those of CF_2Br_2 in which telemerization was a bothersome side reaction.[6]

Similar reactions of CF_2I_2 with internal olefins such as *trans*-4-octene and cyclohexene were also quite successful (eq 5–7). However, its attempted addition to 2,3-dimethyl-2-butene resulted in the exclusive formation of iodoalkene **2**, likely via diversion of the expected radical intermediate by H atom abstraction.

Methods for the dehalogenative conversion of diiodides such as **3**–**7** to cyclopropanes are being pursued as are further studies of the chemistry of CF_2I_2.



(5) (6) (7)

Experimental Section

^{19}F NMR spectra were obtained on a Nicolet NT-300 spectrometer operating at a field of 7 T. Fluorine chemical shifts (ϕ) are reported in parts per million upfield of $CFCl_3$. ^1H and ^{13}C chemical shifts (δ) are reported in parts per million downfield of Me_4Si. All NMR spectra were obtained in $CDCl_3$ at ambient temperature. IR spectra were obtained from samples of neat liquids as capillary films between KBr plates. Mass spectra are reported as m/e (relative intensity, fragment). The compounds darkened upon standing, and consequently combustion analytical data were not obtained.

Preparation of CF_2I_2. Into a 500-mL three-necked flask equipped with distillation head and vacuum Hershberg stirrer were placed 142.4 g of CI_4[2] (0.274 mol) and 69.6 g of HgF_2 (0.292 mol). The flask was closed off with a 125-mL pressure-equalizing addition funnel containing 100 mL of 1,2-dichlorobenzene.[7] The system was evacuated to 50 torr through a −78 °C trap, and the dichlorobenzene was added slowly (exothermic as reactions begin!) until the heterogeneous system was wet enough to stir easily (ca. 80 mL). (In an alternative procedure a solid addition tube was used to slowly add HgF_2 to a stirring solution of CI_4.) Heating at 100 °C produced a dark purple distillate which came over at 50–81 °C (50 torr) into a receiving flask cooled to 0 °C. Distillation ceased after about 45 min.[8] The trap contents and distillate were combined with those from a previous run (0.270 mol of CI_4 and 0.273 mol of HgF_2) and distilled under vacuum: yield 44.8 g (27%);[8] bp 39–41 °C (80 torr). Small amounts of crude CF_2I_2 can be purified (i.e., freed from I_2) as needed by trap to trap distillation under high vacuum through a −10, −40, −78, and −196 °C trap system. Pure CF_2I_2 is found in the −78 °C trap. ^{19}F NMR ϕ −18.6 (s); ^{13}C NMR 2.29 (t, J_{FC} = 378 Hz); MS, 304 (28, M^+), 285 (3.6, CFI_2), 254 (24, I_2), 177 (100, CF_2I), 158 (3.0, CFI), 127 (36, I), 50 (2.2, CF_2); IR 720, 1045, 1095 cm^{-1}. CF_2I_2 has a vapor pressure of 28 torr at 25 °C.

Photolysis of CF_2I_2 in the Presence of 2,3-Dimethyl-2-butene and Mercury. Into a small Carius tube were weighed 0.30 g of CF_2I_2 (0.99 mmol), 1.33 g of 2,3-dimethyl-2-butene (16 mmol), and 0.87 g of Hg (4.4 mmol). The reaction mixture was thoroughly degassed, and the tube was sealed under vacuum. The mixture was photolyzed for 23 h with occasional shaking. Afterward the tube was opened, and all volatile material was vacuum transferred and analyzed by ^{19}F NMR with *m*-bromobenzotrifluoride as an internal standard for yield determination. The product mixture contained 25% 1,1-difluoro-2,2,3,3-tetramethylcyclopropane (**1**) and 29% 4,4-difluoro-4-iodo-2,3,3-trimethyl-1-butene (**2**). Pure samples of each were isolated by preparative gas chromatography (20% dinonyl phthalate on Chromosorb WHP, 20 ft × 0.25 in., 110 °C). **1**: ^1H NMR (δ 1.1, t, J_{HF} = 2 Hz) and ^{19}F NMR (ϕ 149) spectra were identical with those reported for **1**.[9] **2**: ^1H NMR (100 M Hz) δ 5.09, 5.05 (br partially resolved singlets, vinylic, 2 H), 1.85 (midpoint, dd, J = 3.3 Hz, J' = 1.5 H, allylic, 3 H), 1.29 (t, J_{HF} = 0.8 Hz, methyls on C_3, 6 H); ^{19}F NMR ϕ 41.5 (br s); ^{13}C NMR δ 145.5 (br s, C_2), 116.3 (s, C_1), 114.5 (t, J_{FC} = 322 Hz, C_4), 52.7 (t, J_{FC} = 15.9 Hz,

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(7) Other inert, high-boiling solvents (e.g., perfluorodecaline or n-$C_8F_{17}SO_2F$) can also be used.
(8) Higher isolated yields can be obtained by isolating the small amount of CF_2I_2 remaining in the reaction mixture. This can be done by slowly pulling a vacuum above the stirring mixture at room temperature through a −78 °C trap followed by vacuum distillation of the trap contents.
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C_3), 23.1 (t, J_{FC} = 3.7 Hz, methyls on C_3), 21.3 (t, J_{FC} = 3.1 Hz, allylic CH_3 on C_2); IR 575, 770, 860, 925, 1070 (s), 1215, 1385, 1450, 1640 (w, C=C), 2960 cm^{-1}; MS, m/e 259.9882$_2$ ● 0.0027 (M^+, 0.1% of base, ±10.1 ppm), calcd for $C_7H_{11}F_2I$ m/e 259.9873$_6$ (deviation = 0.0008$_6$; +3.3 ppm); other major fragments 133 (71.3, $M^+ - I$), 128 (10.7), 127 (8.0), 113 (21.2), 97 (15.4), 91 (29.1), 85 (11.0), 83 (16.7), 77 (26.3), 73 (33.2), 70 (13.4), 69 (22.0), 67 (16.7), 65 (28.8), 61 (14.1), 57 (35.4), 55 (37.5), 53 (17.8), 51 (11.1), 43 (32.0), 41 (100), 39 (46.3), 29 (13.6), 28 (15.2), 27 (20.9).

Photolysis of CF_2I_2 and Ia without Hg. In the absence of mercury, a photolysis performed as described above showed only 40% conversion of CF_2I_2 and gave a similar product ratio.

Radical Addition of CF_2I_2 to 1-Hexene. Into a 10-mL round-bottomed flask were weighed 0.325 g of CF_2I_2 (1.07 mmol), 1.108 g of 1-hexene (13.2 mmol), and 10 mg of benzoyl peroxide. After refluxing the magnetically stirred solution for 10.5 h, excess olefin was removed by rotary evaporation, and the pale pink residue was purified by flash chromatography,[10] eluting with hexane, to yield 1,1-difluoro-1,3-diiodoheptane (**3**): 0.304 g (73%); ^1H NMR δ 0.95 (t, J = 6 Hz, 3 H), 1.2-3.1 (br m, 6 H), 2.8-3.6 (m, 2 H), 4.32 (quintet, J = 7 Hz, 1 H); ^{19}F NMR ϕ 36.18 (midpoint, AB, J_{AB} = 172 Hz, $\Delta\phi$ AB = 1.75 ppm; downfield F, dd, J_{HF} = 18, 10 Hz; upfield F, dd, J_{HF} = 17, 14 Hz); ^{13}C NMR δ 99.6 (t, J_{FC} = 316 Hz, C_1), 58.2 (t, J = 40 Hz, C_2), 39.2 (s), 31.5 (s), 25.3 (br s, C_3), 21.7 (s), 13.9 (s, C_7); IR 895 (s), 1060, 1165, 2870, 2880, 2930 (s), 2970 (s) cm^{-1}; MS, 388 (1.0, M^+), 261 (4.8, $M^+ - I$), 41 (100, C_3H_5 and many smaller fragments). The ^{19}F NMR showed the product to contain about 3% of the opposite regioadduct 2-(difluoroiodomethyl)-1-iodohexane: ϕ 38.1 (midpoint, AB of d, J_{AB} = 172 Hz, $\Delta\phi$ AB = 1.75, J_{HF} = 10 Hz).

Addition of CF_2I_2 to Methyl Propenoate. A mixture of 1.02 g of methyl propenoate (11.8 mmol, MCB, freshly distilled from phenothiazene onto molecular sieves), 2.15 g of CF_2I_2 (7.07 mmol), about 4 mL of benzene, and 0.1 g of benzoyl peroxide (0.1 mmol) were allowed to react similarly for 19 h at 90-106 °C to yield 36% of unreacted CF_2I_2 plus 1.29 g (47%) of methyl 4,4-difluoro-2,4-diiodobutanoate (**4**): ^1H NMR (100 MHz) δ 4.55 (dd, J = 10, 3.8 Hz, 1 H), 2.84-3.95 (m, 2 H), 3.77 (s, 3 H); ^{19}F NMR ϕ 40.1 (midpoint, AB, J_{AB} = 176 Hz, $\Delta\phi$ AB = 0.3 ppm, J_{HF} = 15 Hz); IR 900, 1075, 1120, 1170, 1195, 1255, 1315 (w), 1360 (w), 1415 (w), 1435 (w), 1735 (s), 2960 (w) cm^{-1}; ^{13}C NMR δ 170.3 (s, C=O), 97.0 (t, J_{FC} = 315 Hz, CF_2I), 54.5 (t, J_{FC} = 21 Hz, CH_2) 53.3 (s, CH_3), 7.8 (t, J_{FC} = 2.4 Hz, CHI); MS, 359 (1.3, M - OCH_3), 331 (0.3, M - CO_2CH_3), 263 (20.8, M - I), 254 (0.8, I_2), 136 (100, M - I), 127 (24.5, I), 77 (27.7, $C_3H_3F_2$), 64 (3.0, $C_2H_2F_2$), 59 (17.3, CO_2CH_3), 31 (13.9, OCH_3 and other fragments), no M^+ observed.

Addition of CF_2I_2 to *trans*-4-Octene. A mixture of 0.70 g of CF_2I_2 (2.3 mmol), 0.81 g of *trans*-4-octene (7.2 mmol), and 0.10 g benzoyl peroxide was allowed to react similarly, yielding a 1:1 mixture of the two possible diasterioisomeric 4-(difluoroidomethyl)-5-iodoctanes **5**: 84%; ^{19}F NMR ϕ 36.6 (midpoint, AB of d, $\Delta\phi$ AB = 3.02 ppm, J_{AB} = 187 Hz; downfield F, d, J_{HF} = 14 Hz; upfield F, d, J_{HF} = 17.5 Hz), 37.5 (midpoint, AB of d, $\Delta\phi$ AB = 3.17 ppm, J_{AB} = 188 Hz; downfield F, d, J_{HF} = 13.5 Hz; upfield F, d, J_{HF} = 15 Hz); ^1H NMR of reaction mixture shows the hydrogens on C_5 at δ 4.45 (multiplets).

Radical Addition of CF_2I_2 to Cyclohexene. A mixture of 1.00 g of CF_2I_2 (3.3 mmol), 1.20 g of cyclohexene (14.6 mmol), and 0.03 g of benzoyl peroxide (0.1 mmol) was allowed to react at 90-97 °C for 20 h to yield 61% of a mixture consisting of 65% *trans*-1-(difluoroiodomethyl)-2-iodocyclohexane (**6**), 28% *cis*-1-(difluoroiodomethyl)-2-iodocyclohexane (**7**), 4% unreacted CF_2I_2, and 3% of an unidentified product (ϕ 42, midpoint, AB, $J \simeq 10$ Hz, $\Delta\phi \simeq 1$ ppm). The major diastereomeric products were isolated by preparative GLC (20% OV-210 on Chromasorb WHP 60/80, 10 ft × $^1/_4$ in., 150 °C: retention times, trans, 27 min; cis, 33 min, some slight decomposition under these GC conditions). **6**: ^{19}F NMR ϕ 34.5 (d, J = 10.3 Hz); ^1H NMR δ 4.27 (ddd, J_{trans} = 8.5 Hz, J'_{trans} = 7.0 Hz, J_{cis} = 4.5 Hz, 1 H, HCI), 1.1-2.5 (complex multiplets, 9 H); ^{13}C NMR δ 108.0 (t, J = 319 Hz, CF_2I), 57.3 (t, J = 16.5 Hz, C_1), 38.3 (s), 27.9 (s), 27.5 (dd, J = 3.6, 2.5 Hz), 26.2 (s), 22.7. **7**: ^{19}F NMR ϕ 42.4 (midpoint, AB, J_{AB} = 172 Hz, $\Delta\phi$ = 5.12; downfield F, d, J_{HF} = 13.6 Hz; upfield F, d, J_{HF} = 12.8 Hz); ^1H NMR δ 4.75 (br s, 1 H, H-CI), 1.1-2.3 (complex multiplets, 9 H); ^{13}C NMR δ 105.7 (dd, J = 321, 320 Hz, CF_2I), 57.5 (t, J = 9.8 Hz, C_1), 37.2 (s), 32.1 (dd, J = 3.7, 2.4 Hz, C_6), 24.8 (s), 23.6 (t, J = 2.4 Hz, C_2), 22.2 (s).

Radical Addition of CF_2I_2 to 2,3-Dimethyl-2-butene. Refluxing 0.56 g of CF_2I_2 (1.8 mmol), 0.86 g of 2,3-dimethyl-2-butene (10 mmol), and 0.02 g of benzoyl peroxide (0.08 mmol) for 24 h gave **2** as the only F-containing product. More than half of the CF_2I_2 was recovered unchanged. The yield was 95% based on converted CF_2I_2 and ^{19}f NMR integration.

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Registry No. 1, 823-25-6; 2, 87970-47-6; 3, 87970-48-7; 4, 87970-49-8; (*R**,*R**)-5, 87970-50-1; (*R**,*S**)-5, 87970-51-2; 6, 87970-52-3; 7, 87970-53-4; CF_2I_2, 1184-76-5; CI_4, 507-25-5; HgF_2, 7783-39-3; 2,3-dimethyl-2-butene, 563-79-1; 1-hexene, 592-41-6; methyl propenoate, 96-33-3; *trans*-4-octene, 14850-23-8; cyclohexene, 110-83-8.

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A Convenient, Mild Method for the Cyclization of 3- and 4-Arylalkanoic Acids via Their Trifluoromethanesulfonic Anhydride Derivatives

Bernard Hulin and Masato Koreeda*

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

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The cyclization reaction of 3- and 4-arylalkanoic acids to the corresponding cyclic ketones has been the subject of intense study for many years.[1] In particular, considerable attention has been focused on the synthesis of 1-tetralone analogues (**3**, n = 2) from 4-arylbutanoic acids in connection with the synthesis of the dihydrodiol and diol epoxide metabolites of carcinogenic polycyclic aromatic hydrocarbons.[2] The cyclization is generally effected either directly by using strong acids such as HF, methanesulfonic acid, and polyphosphoric acid or via the acid chloride, promoted by metal halides such as $AlCl_3$ and $ZnBr_2$.[1-3]

In recent years, activation of certain electrophiles as their trifluoromethanesulfonate (or triflate) derivatives has found widespread application owing to their pronounced leaving-group capabilities.[4] While this triflate activation has been extensively explored in the intermolecular Friedel-Crafts acylation of aromatic coumounds by Effenberger and his co-workers,[5] its intramolecular version has not been reported. In the following, we describe a highly efficient and mild one-pot procedure for the cyclization of 3- and 4-arylalkanoic acids to the corresponding cyclic ketones via their triflic anhydride derivatives **2** (Scheme I).

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