or with sodium borohydride in methanol containing cerium trichloride.[7] The crude mixture of diols **4** and **5** is suitable for the cyclization that is easily performed by means of the acidic resin Amberlyst-15 in a high-dilution condition. The *endo*-**6** and *exo*-**7** are easily separated by flash chromatography. The *endo*-(1*S*,3*S*,5*R*)-**6** is obtained in a 50% overall yield, while the *exo*-(1*S*,3*R*,5*R*)-**7** is obtained in a 34% overall yield in spite of the low selectivity in the reduction of the hydroxy ketone **3** to the *anti*-diol **5**. Both isomers are of high chemical and enantiomeric purity as shown by VPC analyses and polarimetric measurements. The NMR data are in accord with published values.

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer 177 spectrophotometer. ^{1}H nuclear magnetic resonance spectra were recorded in $CDCl_3$ at 90 MHz on a Varian XL 100/15 instrument with tetramethylsilane as the internal standard. Optical rotations were measured with the indicated solvent and at the indicated concentration in a 1-dm cell on a Jasco DIP-181 polarimeter. Gas chromatographic analyses were performed in the following ways: column A, 25 m × 0.32 mm (i.d.) glass capillary column, coated with OV-1 (d_f = 0.4 μm), using a C. Erba apparatus Model 4160 and on-column injection system, carrier gas H_2, μ = 60 cm/s; column B, 25 m × 0.32 mm (i.d.) fused silica capillary column, coated with OV-1701 (d_f = 0.2 μm), using a Dani apparatus Model 6500 and PTV injection system, carrier gas H_2, μ = 54 cm/s; column C, 2 m × 3 mm (i.d.) glass column, packed with 5% SP 1000 on 100/120 Supelcoport, using a Dani Model 3800 apparatus, carrier gas N_2, flow rate 25 mL/min. The (*S*)-DHP was more than 99% enantiomerically pure; the optical purity of the (*R*)-DHP was 98%.

(*S*)-2-Hydroxy-4-(1,3-dithian-2-yl)-8-(1,3-dioxolan-2-yl)-nonane [(*S*)-2]. *n*-BuLi (2.4 M, 10 mL) was added dropwise to a solution of (*S*)-DHP (1.78 g, 10 mmol) in THF (15 mL), stirred at −15 °C under argon. The resulting solution was allowed to warm to 0 °C over 3 h. Freshly distilled 2-(3-chloropropyl)-2-methyl-1,3-dioxolane (2.3 g, 14 mmol) and HMPA (1 mL) were added at 0 °C, and the reaction mixture was stirred overnight at room temperature. Water (50 mL) was added and the resultant mixture extracted twice with ether (100 mL). The combined ether extracts were washed with brine and dried over Na_2SO_4, and the ether was removed in vacuo. The residue was purified by flash chromatography with hexane/ethyl acetate (3:2) as eluent. A 0.15-g portion of unchanged (*S*)-DHP and 2.70 g (9 mmol) of the expected **2** were recovered. The title compound **2** is a dense oil, 98% pure by VPC on column A (4 min at 150 °C, 2.5 °C/min to 230 °C): RT 27.4 min; $[\alpha]^{20}_D$ +17.2° (*c* 1, $CHCl_3$); ^{1}H NMR δ 1.20 (d, *J* = 6 Hz, 3 H), 1.34 (s, 3 H), 1.65 (m, 4 H), 1.75–2.15 (brm, 6 H), 2.9 (m, 4 H), 3.46 (brs, 1 H), 3.98 (s, 4 H), 4.15 (m, 1 H).

(*R*)-2-Hydroxy-4-(1,3-dithian-2-yl)-8-(1,3-dioxolan-2-yl)-nonane [(*R*)-2]. This compound was obtained by the same procedure except from (*R*)-DHP: $[\alpha]^{20}_D$ −16.8 (*c* 1, $CHCl_3$).

(*S*)-2-Hydroxy-4-keto-8-(1,3-dioxolan-2-yl)nonane [(*S*)-3]. A solution of **2** (2.70 g, 9 mmol) in THF (30 mL) and water (6 mL) was stirred at room temperature in the presence of $CaCO_3$ (1.10 g), and $Hg(ClO_4)_2$ (2.5 mL of a 4 M water solution) was added in 10 min. After the resultant solution was stirred an additional 5 min, ether (150 mL) was added and the mixture filtered. The solvents were removed in vacuo to leave 1.72 g of the crude, liquid hydroxy ketone **3**, 93% pure by VPC on column B (1 min at 40 °C, 20 °C/min to 120 °C, 2 min at 120 °C, 2 °C/min to 200 °C): RT 20.0 min; IR (film) 1710 cm^{-1}; ^{1}H NMR δ 1.20 (d, *J* = 6 Hz, 3 H), 1.33 (s, 3 H), 1.66 (m, 4 H), 2.0–2.31 (m, 4 H), 2.5 (br s, 1 H), 3.98 (s, 4 H), 4.23 (m, 1 H).

(*R*)-2-Hydroxy-4-keto-8-(1,3-dioxolan-2-yl)nonane [(*R*)-3]. The compound, prepared by the preceding method, was 95% pure by VPC: $[\alpha]^{20}_D$ −41.7° (*c* 1, $CHCl_3$).

(1*S*,3*S*,5*R*)-1,3-Dimethyl-2,9-dioxabicyclo[3.3.1]nonane (6). The hydroxy ketone (*S*)-**3** (1.70 g) in ether (20 mL) was added to a 0.12 M solution of $Zn(BH_4)_2$ in ether (65 mL) under ice-cooling. The reduction was completed in 30 min. Water (4 mL) was added and the reaction mixture was stirred 30 min. Na_2SO_4 was added for drying, the resulting suspension filtered, and the solvent removed in vacuo. The residue was dissolved in methanol (20 mL) and the methanol evaporated in vacuo three times to liberate the diol from boric esters. The crude, oily diol weighed 1.70 g and was 81% pure, as determined by VPC on column B (same analytical conditions as for the hydroxy ketone **3**). The diol **5** (RT 31.8 min) and the diol **4** (RT 32.3 min) were in a 1 to 9 ratio. The crude mixture of the diols was dissolved in benzene (5 mL) and added in 4 h to a mixture of benzene (5 mL) and pentane (20 mL) with stirring at room temperature in the presence of 50 mg of Amberlyst-15. Stirring was continued for 1 h more, the resin was filtered off, the solvents were cautiously evaporated, and the residue was purified by flash chromatography with pentane/ether (6:1) as the eluent. The fractions containing the same compound were combined, the solvent was evaporated, and the residue was distilled (Kugelrohr) at 100 °C (5.3 kPa), affording 0.78 g (5 mmol) of the (1*S*,3*S*,5*R*)-**6**, 99% pure by VPC on column B [1 min at 40 °C, 20 °C/min to 80 °C, 2 min at 80 °C, 2.5 °C/min to 160 °C; RT 5.7 min] and on column C [8 min at 100 °C, 5 °C/min to 220 °C) RT 5.3 min]: $[\alpha]^{20}_D$ +45.7° (*c* 1, pentane) [lit.[3] $[\alpha]^{20}_D$ +37.5° (*c* 5.4, pentane)]; ^{1}H NMR δ 1.20 (d, *J* = 6 Hz, 3 H), 1.30 (s, 3 H), 1.33–2.30 (brm, 8 H), 3.97 (ddq, *J* = 3.8, 11.2, 6 Hz, 1 H), 4.30 (m, 1 H).

(1*S*,3*R*,5*R*)-1,3-Dimethyl-2,9-dioxabicyclo[3.3.1]nonane (7). $NaBH_4$ (265 mg, 7 mmol) was added portionwise, to an ice-cooled solution obtained by dissolving the hydroxy ketone (*R*)-**3** (1.70 g) in methanol (18 mL) containing $CeCl_3 \cdot 7H_2O$ (7.2 mmol). After the mixture was stirred for 30 min, water (30 mL) was added and the mixture extracted with ether (three 100-mL portions). The ether extracts were washed with brine and dried over Na_2SO_4, and the solvent was removed. The residue, after the methanol treatment as previously described, was a mixture of the diol **5** and the diol **4** in a 2 to 1 ratio as shown by VPC. The crude mixture was cyclized and purified as described before. The two isomers were isolated and distilled. (1*R*,3*R*,5*S*)-**6**: 250 mg (1.6 mmol); 95% pure by VPC; $[\alpha]^{20}_D$ −41° (*c* 1, pentane) [lit.[3] $[\alpha]^{20}_D$ −37.5° (*c* 0.9, pentane)]. (1*S*,3*R*,5*R*)-**7**: 530 mg (3.4 mmol); distilled (Kugelrohr) at 110 °C (5.3 kPa), 98% pure VPC (column B, RT 7.7 min; column C, RT 8.9 min) ; $[\alpha]^{20}_D$ +10.7° (*c* 3, pentane) [lit.[3] $[\alpha]^{20}_D$ +4.7° (*c* 3.2, pentane)]; ^{1}H NMR δ 1.17 (d, *J* = 6 Hz, 3 H), 1.32 (s, 3 H), 1.37–2.27 (brm, 8 H), 4.21 (m, 1 H), 4.60 (m, 1 H).

Registry No. (*S*)-**1**, 86146-06-7; (*R*)-**1**, 91888-93-6; (*S*)-**2**, 109927-88-0; (*R*)-**2**, 109927-89-1; (*S*)-**3**, 109927-90-4; (*R*)-**3**, 109927-91-5; **4** (isomer 1), 109927-92-6; **4** (isomer 2), 109927-93-7; **5** (isomer 1), 109927-94-8; **5** (isomer 2), 109927-95-9; (1*S*,3*S*,5*R*)-**6**, 76740-35-7; (1*R*,3*R*,5*S*)-**6**, 76740-34-6; (1*S*,3*R*,5*R*)-**7**, 76334-10-6; 2-(3-chloropropyl)-2-methyl-1,3-dioxolane, 5978-08-5.

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Room-Temperature Fluorination of 1-Phenylacetylenes with Cesium Fluoroxysulfate

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It is of importance from a chemical and pharmaceutical point of view that only a limited number of reagents are able to introduce fluorine under mild conditions at room temperature.[1] It has been demonstrated that $CsSO_4F$ reacts with various organic molecules; however, the effectiveness of the fluorination is influenced by both the structure of the molecule and the appropriateness of the reaction conditions.[2-6]

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Table I. Effect of the Acetylene Structure and Free-Radical Inhibitors on the Product Distribution Observed by Reactions of $CsSO_4F$ in Methanol at 22 °C

	relative yields[a]							
acetylene R	2	3	4	5	6	7	8	2 + 3
C_6H_5	40	60						100
H	50	50						100
$C(CH_3)_3$	54	46						100
$CH_2CH_2CH_3$	31	25		25	5	10	4	56
$CH_2CH_2CH_3$[c]	57	35		8	<1	<1	<1	92
CH_3	20	19	3	26	6	17	9	39
CH_3[b]	27	28	2	14	4	16	9	55
CH_3[c]	41	41	1	12	<1	<1	5	82

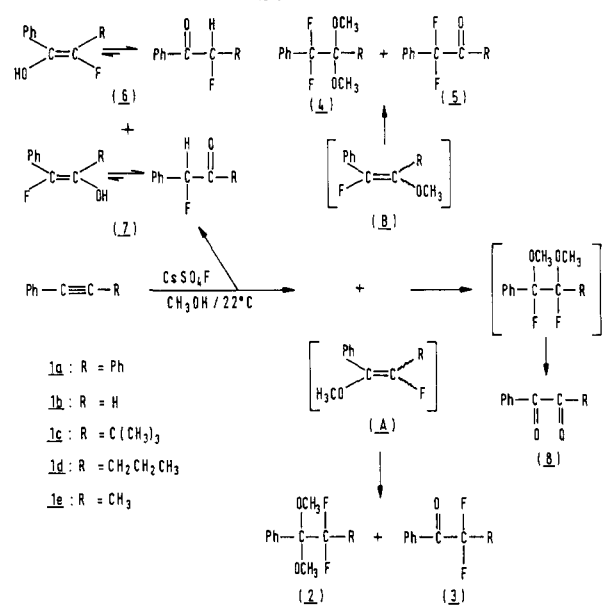
[a] Product distributions determined by ^{19}F NMR and GLC. [b] Acetylene/nitrobenzene, 1 mmol/0.1 mmol. [c] Acetylene/nitrobenzene, 1 mmol/1 mmol.

Electrophilic addition of halogens to olefins has been the subject of considerable study, while the analogous additions to acetylenic systems have received less attention. A structure relationship exists between carbon–carbon double bonds and triple bonds where the reactivities of the two systems toward electrophilic reagents may differ by as much as a factor of 10^5. This difference has been explained in terms of the ease of formation of carbonium ions and vinyl cations.[7] We have already demonstrated that $CsSO_4F$ reacts with various olefins;[8] however, in view of the aforementioned consideration, it was not certain that $CsSO_4F$ would react with phenyl-substituted acetylenes. On the other hand, the addition across the triple bond may undergo an accompanying substitution reaction on the phenyl ring, if the ease of fluorination of benzene derivatives of $CsSO_4F$ is taken into account.[2-4]

Results and Discussion

Valuable information about the reactivity of a new fluorinating agent can be obtained by studying its reactions with organic molecules that have already been investigated with other reagents. Therefore, an obvious place to begin out study was with 1,2-diphenylethyne, which had previously been tested with many fluorination reagents. The low-temperature reaction of fluorine in methanol[9] resulted in the formation of the following three products: 1,1,2,2-tetrafluoro-1,2-diphenylethane, 1,1,2-trifluoro-2-methoxy-1,2-diphenylethane (the major product), and 1,1-difluoro-2,2-dimethoxy-1,2-diphenylethane, while the low-temperature reaction with fluoroxytrifluoromethane led to 1,2,2-trifluoro-1,2-diphenyl-1-(trifluoromethoxy)ethane as the major product accompanied by many other products.[10] A similar reaction with trifluoroacetyl hypofluorite gave 2-fluoro-1,2-diphenylethanone and benzil as the main products,[11] while room-temperature fluorination with xenon difluoride depended on the catalyst used: 1,1,2,2-tetrafluoro-1,2-diphenylethane was formed in the presence of hydrogen fluoride,[12] but six products resulted in the reaction catalyzed by trifluoroacetic acid.[13] As should be evident, the structure of the fluorinating agent plays a major role in the fluorination of acetylenes.

Scheme I



Room-temperature reaction of 1,2-diphenylacetylene with cesium fluoroxysulfate in methanol resulted in the formation of two products (**2** and **3**), which were isolated by preparative GLC and characterized on the basis of spectroscopic data. In a separate experiment we have excluded the possibility of the transformation of 1,1-difluoro-2,2-dimethoxy-1,2-diphenylethane (**2**) to 2,2-difluoro-1,2-diphenylethanone (**3**) or vice versa under the reaction conditions. It is evident that the reactivity of $CsSO_4F$ differs markedly from all other fluorinating reagents previously studied. Further, we have studied the regioselectivity of fluorine introduction into phenylacetylenes and have found that the entering methoxy group followed Markovnikoff's type regioselectivity in the case of 1-phenylacetylene (Scheme I, **1b**) and 1-phenyl-2-*tert*-butylacetylene (**1c**), while reactions became more complex in the case of 1-phenyl-1-propyne (**1e**) and 1-phenyl-1-pentyne (**1d**). The formation of products **2** and **3** could be explained with the intermediate formation of a methoxy fluoro olefin (Scheme I, A), which was not observed. The tendency of further transformation to α-difluoro ketones has already been demonstrated by the fluorination of 1-alkoxy- and 2-alkoxynaphthalenes with $CsSO_4F$.[4,6]

The complex reaction mixtures obtained in the fluorinations of **1d** and **1e** were analyzed by GLC and ^{19}F NMR. In the case of **1d**, six products were formed, while with **1e**,

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seven products resulted. The products were isolated by preparative GLC, and their structures were determined on the basis of spectroscopic data. Mass spectral fragmentations were especially useful in the differentiation of the regioselectivity of the fluorination. The formation of the products following Markovnikoff's type regioselectivity could be explained by the formation of carbonium ion intermediates, while other products could be ascribed to the formation of radical intermediates. To differentiate between intermediates, we have studied the effect of the addition of either nitrobenzene or 2,4,6-tri-*tert*-butylphenol as free-radical scavenger, and as evident from Table I, the presence of products **4**, **6**, and **7** was almost excluded, while the amounts of products **5** and **8** were strongly diminished. Possible reaction pathways leading to the products are presented in the scheme, and, as several times before, the importance of the structure of the substrate in the course of fluorine introduction is once again demonstrated.

Experimental Section

IR spectra were recorded with a Perkin-Elmer 277B spectrometer and ^1H and ^{19}F NMR spectra by a JEOL-JNM-PS 100 instrument, with Me_4Si or CCl_3F as the internal reference. Mass spectra and high-resolution measurements were taken on a CEC-21-110 spectrometer. Gas–liquid partition chromatography was carried out on Varian Aerograph Models 2700 and 3700 and TLC on Merck PSC-Fertigplatten silica gel F-254.

Fluorination of 1-Phenylalkynes. A 2-mmol sample of alkyne (**1a–1e**) was dissolved in 8 mL of methanol, and with stirring at room temperature, 6 mmol of $CsSO_4F$ was added slowly over a period of 10 min. The reaction mixture was then stirred at room temperature for an additional hour, 40 mL of CH_2Cl_2 was added, the unsoluble products were filtered off, the filtrate was washed with water, the organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The crude reaction mixture was analyzed by ^{19}F NMR and GLC.

Fluorination of 1,2-Diphenylethyne (1a). The crude reaction mixture was separated by preparative GLC (SE-30 10%, Chromosorb W AW 60/80, T = 175 °C).

1,1-Difluoro-2,2-dimethoxy-1,2-diphenylethane (2a):[9] 23% of oily product; NMR δ_F −106.3 (s), δ_{OCH_3} 3.35 (s, 6 H), δ_H 7.1 (m, 10 H); mass spectrum, m/e 247 ($M^+ - OCH_3$, 7), 185 (5), 152 (11), 151 (100), 127 (16), 106 (6), 105 (73), 91 (10), 77 (52).

1,1-Difluoro-1,2-diphenylethanone (3a):[9] 32% of oily product; NMR δF −97.5 (s), δH 7.4–7.9 (m); mass spectrum, m/e 232 (M^+, 0.5), 127 (11), 106 (8), 105 (100), 77 (50).

Fluorination of 1-Phenylethyne (1b). The crude reaction mixture was separated by preparative GLC (DEGS 8%, Chromosorb W AW 60/80, T = 130 °C).

1,1-Difluoro-2,2-dimethoxy-2-phenylethane (2b):[9] 25% of oily product; NMR δ_F −133.2 (d, $^2J_{FH}$ = 61, 5 Hz), δ_{OCH_3} 3.4 (s, 6 H), δ_H 5.82 (t, J = 60.0 Hz, 1 H), δ_H 7.4 (m, 5 H); mass spectrum, m/e 202 (M^+, 0.2), 171 (20), 152 (10), 151 (100), 109 (20), 105 (65), 91 (25), 77 (63).

2,2-Difluoro-1-phenylethan-1-one (3b):[9] 26% of oily product; NMR δ_F −123.5 (d, $^2J_{FH}$ = 57 Hz), δ_H 6.25 (t, J = 57 Hz, 1 H), δ_H 7.0–8.0 (m, 5 H); mass spectrum, m/e 156 (M^+, 3), 106 (9), 105 (100), 77 (76), 51 (71).

Fluorination of 1-Phenyl-2-*tert*-butylethyne (1c). The crude reaction mixture was separated by preparative GLC (OV 17 10%, Chromosorb W AW 60/80, T = 190 °C).

1,1-Difluoro-2,2-dimethoxy-1-*tert*-butyl-2-phenylethane (2c): 23% of oily product; NMR δ_F −114.0 (br s), δ_{CH_3} 0.8 (s, 9 H), δ_{OCH_3} 3.3 (s, 6 H), δ_H 7.3–7.7 (m, 5 H); mass spectrum calcd for $C_{13}H_{17}OF_2$ ($M^+ - OCH_3$) m/e 227.1247, found m/e 227.1245; m/e 227 ($M^+ - OCH_3$, 4), 201 (5), 152 (11), 151 (100), 105 (31), 91 (10), 77 (28), 57 (121), 51 (18).

2,2-Difluoro-2-*tert*-butyl-1-phenylethan-1-one (3c): 19% of oily product; NMR δ_F −111.0 (br s), δ_{CH_3} 1.2 (s, 9 H), δ_H 7.5–8.05 (m, 5 H); mass spectrum calcd for $C_{12}H_{14}OF_2$ m/e 212.1013, found m/e 212.1015; m/e 212 (M^+, 2), 156 (4), 139 (8), 106 (9), 105 (100), 78 (6), 77 (90), 65 (9), 57 (18), 51 (29).

Fluorination of 1-Phenyl-1-pentyne (1d). The crude reaction mixture was separated by preparative GLC (DEGS 12%, Chromosorb W AW 80/100, T = 100–160 °C).

1-Phenyl-1,1-dimethoxy-2,2-difluoropentane (2d): 12% of oily product; NMR δ_F −110.5 (t, $^3J_{FH}$ = 19.5 Hz), δ_{CH_3} 0.85 (t, J = 6 Hz, 3 H), δ_{CH_2} 1.6 (m, 4 H), δ_{OCH_3} 3.35 (s, 3 H), δ_H 7.4–8 (m, 5 H); mass spectrum calcd for $C_{12}H_{15}OF_2$ ($M^+ - OCH_3$) m/e 213.1091, found m/e 213.1093; m/e 213 ($M^+ - OCH_3$, 8), 152 (11), 151 (100), 105 (20), 91 (8), 77 (15).

1-Phenyl-2,2-difluoropentan-1-one (3d):[14] 10% of oily product; NMR δ_F −100.0 (t, $^3J_{FH}$ = 18 Hz), δ_{CH_3} 0.85 (t, J = 6 Hz, 3 H), δ_{CH_2} 1.6 (m, 4 H), δ_H 7.4–8.2 (m, 5 H); mass spectrum calcd for $C_{11}H_{12}OF_2$ m/e 198.0856, found m/e 198.0853; m/e 198 (M^+, 8), 106 (10), 105 (100), 77 (38), 51 (12), 43 (5).

1-Phenyl-1,1-difluoropentan-2-one (5d): 9% of oily product; NMR δ_F −106.5 (s), δ_{CH_3} 0.85 (t, 3 H), δ_{CH_2} 1.2 (m, 2 H), δ_{CH_2} 2.8 (t, 2 H), δ_H 7.3 (m, 5 H); mass spectrum calcd for $C_{11}H_{12}OF_2$ m/e 198.0856, found m/e 198.0858; m/e 198 (M^+, 10), 127 (70), 121 (35), 77 (38), 71 (100), 51 (12), 43 (90).

1-Phenyl-2-fluoropentan-1-one (6d):[15] 2% of oily product; NMR δ_f −191 (dm, J = 50 Hz); mass spectrum calcd for $C_{11}H_{13}OF$ m/e 180.0950, found m/e 180.0954; m/e 180 (M^+, 15), 106 (10), 105 (100), 77 (50), 51 (25).

1-Phenyl-1-fluoropentan-2-one (7d): 2% of oily product; NMR δ_F −187.2 (d, $^2J_{FH}$ = 52.5 Hz); mass spectrum calcd for $C_{11}H_{13}OF$ m/e 180.0950, found m/e 180.0948; m/e 180 (M^+, 12), 109 (25), 77 (20), 71 (100), 51 (10), 43 (85).

1-Phenylpentane-1,2-dione (8d): 0.5% of oily product; mass spectrum calcd. for $C_{11}H_{12}O_2$ m/e 176.0837, found m/e 176.0835; m/e 176 (M^+, 8), 106 (8), 105 (100), 77 (50), 71 (15), 43 (30).

Fluorination of 1-Phenyl-1-propyne (1e). The crude reaction mixture was separated by preparative GLC (DEGS 10%, Chromosorb W AW 60/80, T = 90–130 °C):

1-Phenyl-1,1-dimethoxy-2,2-difluoropropane (2e):[9] 10% of oily product; NMR δ_F −102.8 (q, $^3J_{FH}$ = 18 Hz), δ_{CH_3} 1.4 (t, 3 H), δ_{OCH_3} 3.4 (s, 6 H), δ_H 7.15–7.4 (m, 5 H); mass spectrum, m/e 185 ($M^+ - OCH_3$, 12), 152 (10), 151 (100), 105 (44), 91 (16), 77 (44), 65 (14), 59 (10), 51 (17).

1-Phenyl-2,2-difluoropropan-1-one (3e):[9] 10% of oily product; NMR δ_F −93.5 (q, $^3J_{FH}$ = 21 Hz), δ_{CH_3} 1.9 (t, 3 H), δ_H 7.5–8.1 (m, 5 H); mass spectrum, m/e 170 (M^+, 5), 106 (10), 105 (100), 77 (72), 65 (5), 51 (21).

1-Phenyl-1,1-difluoropropan-2-one (5e):[16] 15% of oily product; NMR δ_F −108.7 (br s), δ_{CH_3} 2.25 (br s, 3 H), δ_H 7.45 (m, 5 H); mass spectrum calcd for $C_9H_8OF_2$ m/e 170.0543, found m/e 170.0545; m/e 170 (M^+, 15), 128 (10), 127 (100), 77 (48), 51 (38), 50 (18), 43 (70).

1-Phenyl-1-fluoropropan-2-one (7e): 9% of oily product; NMR δ_F −183 (dq, $^2J_{FH}$ = 51 Hz, $^4J_{FH}$ = 4.5 Hz), δ_{CH_3} 2.25 (d, 3 H), δ_H 5.65 (d, J = 51 Hz, 1 H), δ_H 7.45 (m, 5 H); mass spectrum calcd for C_9H_9OF m/e 152.0637, found m/e 152.0639; m/e 152 (M^+, 20), 110 (8), 109 (100), 89 (6), 83 (22), 63 (12), 57 (12), 43 (70).

1-Phenylpropane-1,2-dione (8e): 5% of oily product; NMR δ_{CH3} 2.5 (s, 3 H), δ_H 7.5–8.0 (m, 5 H); mass spectrum calcd for $C_9H_8O_2$ m/e 148.0524, found m/e 148.0527; m/e 148 (M^+, 8), 106 (8), 105 (100), 77 (90), 43 (25).

1,1-Difluoro-1-phenyl-2,2-dimethoxypropane (4e) and 1-phenyl-2-fluoropropan-1-one (6e) were isolated as a mixture containing 29% of **4e** and 71% of **6e**; the mass spectrum of the mixture with their characteristic fragmentations clearly proved the presence of both products. **4e**: MS, m/e 185 ($M^+ - OCH_3$), 128, 127 ($PhCF_2$), 89 ($CH_3C(OCH_3)_2$). **6e**: MS, m/e 152 (M^+), 105 (PhCO), 77 (Ph). **4e**: NMR δ_F −108 (br s), δ_{CH_3} 1.3 (br s, 3 H), δ_{OCH_3} 3.3 (s, 6 H), δ_H 7.5 (m, 5 H). **6e**: NMR δ_F −183.5 (dq, $^2J_{FH}$ = 51 Hz, $^3J_{FH}$ = 25.5 Hz), δ_{CH_3} 1.7 (dd, 3 H), δ_H 5.75 (dq, 1 H), δ_H 7.7–8.1 (m, 5 H).

Effect of Free-Radical Inhibitors on the Fluorination of 1d and 1e. 1 mmol of alkyne (**1d** or **1e**) and 0.1 mmol or 1.0 mmol of nitrobenzene or 2,4,6-tri-*tert*-butylphenol were dissolved in 4 mL of methanol, and with stirring at 22 °C, 3 mmol of $CsSO_4F$ was added slowly over a period of 10 min. The reaction mixture was then stirred at room temperature for an additional hour, and after the usual workup, the crude reaction mixture was analyzed

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by ^{19}F NMR and GLC. Products **4**, **6**, and **7** almost disappeared, while the amounts of products **5** and **8** were strongly diminished. The effect of the free-radical scavengers is evident from the table.

Registry No. **1a**, 501-65-5; **1b**, 536-74-3; **1c**, 4250-82-2; **1d**, 4250-81-1; **1e**, 673-32-5; **2a**, 14210-91-4; **2b**, 14210-92-5; **2c**, 110097-44-4; **2d**, 110097-45-5; **2e**, 14320-36-6; **3a**, 365-01-5; **3b**, 395-01-7; **3c**, 110097-46-6; **3d**, 58534-47-7; **3e**, 703-17-3; **4e**, 110097-47-7; **5d**, 110097-48-8; **5e**, 29548-91-2; **6d**, 29114-66-7; **6e**, 21120-36-5; **7d**, 110097-49-9; **7e**, 21120-43-4; **8d**, 20895-66-3; **8e**, 579-07-7.

Computation of the Structures of the Phenyl and Benzyl Radicals with the UHF Method

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In a recent note Pacansky, Liu, and DeFrees[1] reported computations on the structures of the phenyl and benzyl radicals. The results were obtained by using the restricted open-shell Hartree–Fock method (ROHF), and they were based on a slightly improved version of the GAUSSIAN 82 program package,[2] making use of 4-31G basis sets. It was noted that the use of the corresponding unrestricted Hartree–Fock method (UHF) produces results with S^2 expectation values that are considerably larger than $^3/_4$. Such values imply a certain amount of spin contamination, and it was therefore argued that the UHF method is not appropriate for calculating the structures of the phenyl and benzyl radicals.

Farnell, Pople, and Radom[3] compared the geometries derived from UHF and ROHF computations for a set of small molecules. It was found that the ROHF results are usually in better agreement with experimental data than the UHF results, especially when the spin contamination in the UHF function is significant. Improving the quality of the basis sets in the computation leads to a decrease in the spin contamination in the UHF function and to a better agreement between the UHF and the ROHF geometries.

It was also noted by Farnell, Pople, and Radom[3] that the UHF method is more convenient than the ROHF method. We had similar experiences. We found that there are many situations where the UHF computations converge, while the ROHF computations do not converge. We feel therefore that it may be of interest to compare the geometries of the phenyl and benzyl radicals derived by means of the UHF procedure with the geometries derived by Pacansky, Liu, and DeFrees[1] by means of the ROHF method. If the two sets of geometries turn out to be similar, then we might be encouraged to use the UHF procedure also for geometry predictions in situations where the ROHF method does not converge.

In order to investigate the matter we performed a set of structure calculations of the phenyl and benzyl radicals with the GAUSSIAN 82 program package,[2] using the UHF method. In the case of the phenyl radical we used the 6-31G basis set and in the case of the benzyl radical we used the 4-31G basis set. Those are the largest basis sets for which the UHF computations converge. We compare our results with the structures that were reported in ref 1 using the ROHF procedure. Here the 4-31G basis set was used in both the phenyl and the benzyl computations.

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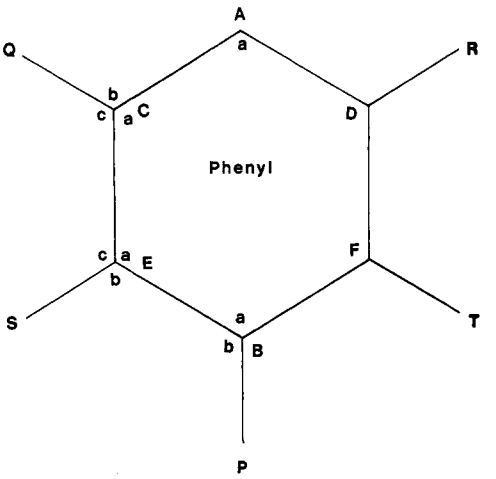

Figure 1. Structure and definitions of bond lengths and bond angles of the phenyl radical.

Table I. Bond Lengths and Bond Angles of the Phenyl Radical Obtained from a UHF Computation with a 6-31G Basis Set and the Same Quantities Obtained from a Previously Reported ROHF Computation with a 4-31G Basis Set[1] (Bond Lengths and Bond Angles Defined in Figure 1)

	UHF	ROHF
	Bond Lengths, Å	
AC	1.392	1.371
BE	1.406	1.387
CE	1.404	1.390
BP	1.073	1.072
CQ	1.072	1.071
ES	1.073	1.072
	Bond Angles, Deg	
a_A	124.5	124.8
a_B	120.8	120.6
a_C	117.3	117.2
a_E	120.0	120.1
b_B	119.6	119.7
b_C	121.6	121.7
b_E	120.0	120.1

Table II. Bond Lengths and Bond Angles of the Benzyl Radical Derived from a UHF Computation with a 4-31G Basis Set and the Same Quantities Derived from a Previously Reported ROHF Computation with a 4-31G Basis Set[1] (Bond Lengths and Bond Angles Are Defined in Figure 2)

	UHF	ROHF
	Bond Lengths, Å	
AC	1.426	1.396
BE	1.402	1.384
CE	1.389	1.380
AG	1.403	1.447
BP	1.072	1.072
CQ	1.073	1.073
ES	1.072	1.072
GU	1.072	1.070
	Bond Angles, Deg	
a_A	117.4	118.0
a_B	119.7	119.6
a_C	121.1	120.9
a_E	120.4	120.3
a_G	118.5	118.2
b_A	121.3	121.0
b_B	120.2	120.2
b_C	118.9	119.3
b_E	119.8	120.0
b_G	121.3	120.9

The various results for the phenyl radical are reported in Table I, and the results for the benzyl radical are reported