Oxidation of fluoroalkyl-substituted allylic alcohols: a synthesis of fluorinated α,β-epoxyketones

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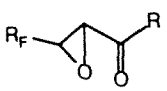
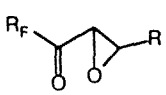
Fluoroalkyl-substituted allylic alcohols are readily and selectively oxidized at the hydroxyl group with the Swern or Dess—Martin reagents to give α,β-unsaturated ketones, and on treatment with *m*-chloroperbenzoic acid or *tert*-butyl hydroperoxide they are oxidized to the corresponding epoxyalcohols. The latter are oxidized by Swern or Dess—Martin reagents at the hydroxyl group to α,β-epoxyketones, which form hydrates stable under the conditions of isolation.

Key words: fluoroalkyl-substituted allylic alcohols, epoxyalcohols, α,β-unsaturated ketones, oxidation of secondary alcohols, epoxidation.

α,β-Epoxyketones are valuable intermediate compounds in organic synthesis because they are readily synthesized and exhibit diverse reactivity.[1—3] The introduction of fluorine-containing substituents into α,β-epoxyketones can substantially extend the synthetic applications of this class of compounds, owing to the theoretical and practical significance of organofluorine derivatives. Previously[4,5] we prepared α,β-epoxyketones (**1**) containing polyfluoroalkyl substituents in the β-position.



1



2

The purpose of the present work is to develop approaches to the synthesis of isomeric α,β-epoxyketones (**2**) in which the fluoroalkyl substituent is attached to the carbonyl carbon atom.

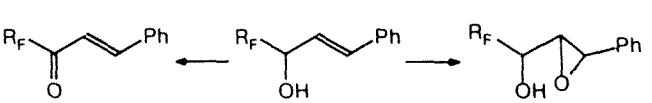
Results and Discussion

The main methods for the synthesis of α,β-epoxyketones are the Darzens reaction[1,2] and epoxidation of α,β-unsaturated ketones with hydrogen peroxide in an alkaline medium.[1,2] As regards the applicability of the Darzens condensation to the synthesis of compounds **2**, an analysis of the published data[1] makes it possible to predict the unsuitability of this reaction, due to the unfavorable distribution of the electronic factors between the carbonyl component (aldehyde) and the methylene component (fluoroalkyl halomethyl ketone).

Previously we successfully used the second of the methods mentioned above to synthesize epoxyketones **1**.[4] To apply this method to the preparation of compounds **2**, one needs the corresponding α,β-unsaturated ketones. The most facile route for preparing α,β-unsaturated ketones (**3**) that contain a fluoroalkyl substituent at the carbonyl carbon atom is oxidation of the corresponding allyl alcohols (**4**). Previously the oxidation of these alcohols into α,β-unsaturated ketones was carried out with MnO_2[6] or with the Dess—Martin reagent (**5**)[7]. We carried out this reaction with the Swern reagent ($DMSO/(COCl)_2/NEt_3$) (**6**) for the first time[8] and also showed that reagent **5** is a promising oxidant in this particular case (Scheme 1, Table 1). We found that oxidation with either of this reagents is very quick (15—20 min). The advantages of the latter are that it is one-component and that the reaction can be conducted at room temperature. Spectral data indicate that the *trans*-configuration of the double bond is retained during the oxidation.

However, our attempts to epoxidate the resulting compounds **3a,b** with hydrogen peroxide in an alkaline medium were unsuccessful. In our opinion, this is due to the possibility of haloform decomposition peculiar to

Scheme 1



3a,b **4a,b** **9a,b**

a: $R_F = CF_3$; **b**: $R_F = C_3F_7$.

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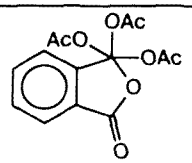
Table 1. Oxidation of fluorine-containing allyl alcohols

Compound	Oxidizing reagent	Reaction temperature / °C	Reaction time / h	Product	Yield (%)
4a	**6**	−60	0.5	**3a**	84
	7	20	10	**9a**	90
	8	20	24	**9a**	89
4b	5*	20	0.3	**3b**	94
	7	20	15	**9b**	94
	8	20	15	**9b**	88

* **5** =



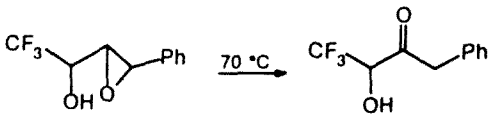
ketones containing fluoroalkyl substituents at the carbonyl carbon atom.[9]

In view of the foregoing, we tried out an alternative approach based on epoxidation and subsequent oxidation of alcohols **4**. To accomplish the first stage, *viz.*, the transformation of the C=C double bond into an epoxide ring, we studied two reagents that are most frequently used for the similar transformation in the hydrocarbon series, namely, *m*-chloroperbenzoic acid (**7**)[10] and *tert*-butyl hydroperoxide in the presence of vanadyl acetylacetonate (**8**).[11] Both reagents proved to be quite suitable, and the use of them led to the formation of fluoroalkyl-containing epoxyalcohols (**9**) in high yields (Scheme 1, Table 1).

In general, reagent **7** is preferred, since it is safer, the reaction time in this case is shorter, and the product yields are somewhat higher. However, in both cases, epoxidation occurs much more slowly than that with the hydrocarbon analogs,[11] probably because of the decrease in the electron density at the C=C bond due to the inductive effect of the fluoroalkyl substituent.

The ^1H and ^{13}C spectra exhibit two groups of signals corresponding to the two diastereomeric alcohols **9**; however, each of the isomers has the *trans*-configuration of the epoxide ring, as indicated by the value of the spin-spin coupling constant of the oxirane protons, which is equal to 2.0—2.1 Hz (this constant for the analogous trichloromethyl-substituted alcohols is 1.95 Hz).[12] Thus, both versions of the reaction are stereospecific. It should be noted that we did not separate these diastereomers, since during their subsequent oxidation to α,β-epoxyketones **2**, one of the asymmetric carbon atoms disappears.

Epoxyalcohols **9** proved to be unstable during heating and isomerized into carbonyl compounds. For example, in one of the experiments in which we attempted to obtain compound **9a** at 70 °C, the corresponding α-hydroxyketone (**10a**) was isolated.

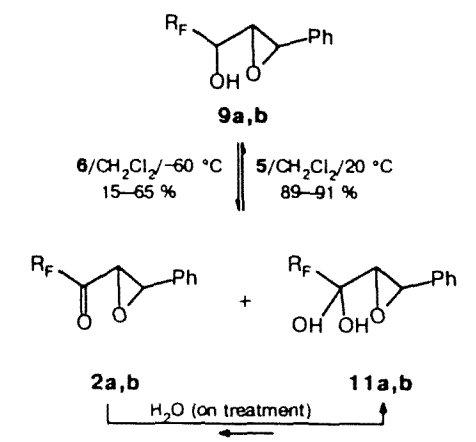


9a **10a**, 22 %

Interpretation of the spectral characteristics of product **10a** deserves special attention due to the fact that our results do not agree with the data reported previously for this compound.[13] Its IR spectrum exhibits two bands corresponding to the stretching vibrations of the OH group (3410 and 3340 cm^{-1}) and a band at 1750 cm^{-1}, associated with the vibrations of the C=O group in aliphatic ketones. The signals of the benzyl protons in the ^1H NMR spectrum (100 MHz) constitute an AB-system at 3.96 ppm (diastereotopism), whereas in the paper cited, a singlet at 3.87 ppm has been reported for $PhCH_2$.

The second stage on the way from alcohols **4** to epoxyketones **2** is oxidation of the hydroxyl group to the keto group. We used reagents **5** and **6**, which showed themselves to advantage in the oxidation of allyl alcohols **4** into unsaturated ketones **3**, as oxidants. Compounds **2a,b** mixed with their hydrates (**11a,b**) were obtained for the first time (Scheme 2).

Scheme 2



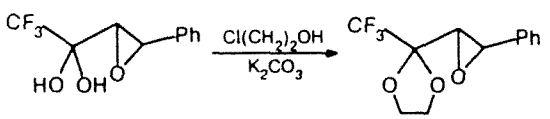
The reaction with either of the reagents occurs quickly (~15 min), but reagent **5** is preferred, since it ensures higher yields and requires simpler experimental conditions.

The ability of compounds **2** to form stable hydrates is beyond doubt. Analogous hydrates were reported for similar chlorine-containing α,β-epoxyketones.[14] It is also known that trifluoromethylketones containing a heteroatomic substituent (NR_2, OR, SR) in the α-position form very stable hydrates stabilized by an intramolecular hydrogen bond, as indicated by X-ray diffraction data.[15]

Whereas compound **2a** exists exclusively as hydrate **11a** (the absence of C=O absorption in the IR spectrum), compound **2b** exists mostly as form **11b** with a small admixture of the free keto-form **2b** (the band of medium intensity at 1760 cm^{-1}), which is also in agreement with the known fact that the ability to undergo hydration decreases as the length of the fluoroalkyl substituent increases.[9]

Compounds **11a,b** are unstable during storage and decompose over a period of one week yielding a complex mixture of products. In the presence of acetic acid in chloroform, decomposition occurs already over a period of 1 day.

We additionally confirmed the structure of compound **11a** by preparing its ethylene ketal derivative **12a** by a procedure used for fluorine-containing ketones.[16]



11a **12a**

The IR spectrum of compound **12a** exhibits no absorption bands for the OH and C=O groups. The ^1H NMR spectrum, in addition to the four-proton multiplet of the dioxolane protons and the singlet of the Ph group, contains two doublets due to the epoxide protons with a spin-spin coupling constant of 2.11 Hz, which corresponds to their *trans*-configuration. Unlike the starting **11a**, derivative **12a** is stable during storage.

Experimental

The ^1H NMR spectra of the obtained compounds were recorded on a Tesla BS-567 A spectrometer (100 MHz) and a Bruker AM-300 spectrometer (300 MHz) using tetramethylsilane as the internal standard. The ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer (75 MHz) using tetramethylsilane as the internal standard. The ^{19}F NMR spectra were run on a Tesla BS-567 A instrument (94.1 MHz) using C_6F_6 as the internal standard. IR spectra were obtained on a Specord IR-75 instrument in Vaseline oil for solid samples or for thin films in the case of liquids. TLC was performed on Silufol UV-254 plates, and visualization was carried out by UV irradiation, a solution of $KMnO_4$, or a solution of KI in glacial AcOH.

Compounds **4a,b** were prepared by a previously reported procedure;[17] compound 7 was obtained by a known procedure;[18] and *t*-BuOOH was also prepared by a previously reported procedure.[19] DMSO, CH_2Cl_2, and Et_3N were dehydrated by known methods. Freshly distilled oxalyl chloride was used. Reagent **5** was prepared according to a reported procedure.[20] The other reagents and solvents were used without purification.

1,1,1-Trifluoro-4-phenyl-3-buten-4-one (3a). A solution of oxalyl chloride (0.47 mL, 5.5 mmol) in 12.5 mL of CH_2Cl_2 was placed into a three-necked flask equipped with a thermometer, a magnetic stirrer, and two dropping funnels with calcium-chloride tubes, and cooled to −60 °C. A solution of DMSO (0.85 mL, 12.0 mmol) in 2.5 mL of CH_2Cl_2 was added from one of the funnels, the mixture was stirred for 10 min, and then a solution of compound **4a** (1.01 g, 5.0 mmol) in 5 mL of CH_2Cl_2 was added through the other funnel. The velocity of the addition of both reagents was controlled in such a way that the temperature of the reaction mixture was not higher than −60 °C. After 15 min, NEt_3 (3.48 mL, 25.0 mmol) was added dropwise, the mixture was allowed to warm up to ~20 °C, 15 mL of water was added, and 10 min later, the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2×10 mL), and the combined extract was washed successively with dilute HCl, water, a dilute solution of $NaHCO_3$, and water and dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on a column using a hexane—chloroform (3:1) mixture as the eluent to give 0.84 g (84 %) of compound **3a** as a light brown liquid. IR, ν/cm^{-1}: 1720 (C=O), 1610 (C=C). ^1H NMR ($CDCl_3$), δ: 7.39 (d, J = 16.0 Hz, 1 H, —CH=), 7.48—7.92 (m, 5 H, Ph), 8.06 (d, J = 16.0 Hz, 1 H, —CH=). ^{19}F NMR ($CDCl_3$), δ: 84.9 (s, 3 F, CF_3).

4,4,5,5,6,6,6-Heptafluoro-1-phenyl-1-buten-3-one (3b). Compound **4b** (1.14 g, 3.77 mmol) and 30 mL of anhydrous CH_2Cl_2 were placed into a one-necked flat-bottom flask. Reagent **5** (2.08 g, 4.90 mmol) was added in one portion with stirring, and the reaction was monitored by TLC using CH_2Cl_2 as the eluent. When the starting **4b** disappeared (~20 min), the reaction mixture was poured into a mixture of 50 mL of ether and 100 mL of a saturated solution of $NaHCO_3$, containing $Na_2S_2O_5 \cdot 5H_2O$ (8.51 g, 34.3 mmol). The precipitate dissolved after 10 min of stirring. The organic layer was separated, and the aqueous layer was extracted with ether (3×10 mL). The combined extract was washed with brine and dried with $MgSO_4$. Evaporation of the solvent gave 1.07 g (94 %) of compound **3b** as a light yellow liquid. ^1H NMR ($CDCl_3$), δ: 7.29 (d, J = 15.85 Hz, 1 H, —CH=), 7.39—7.84 (m, 5 H, Ph), 8.00 (d, J = 15.85 Hz, 1 H, —CH=).

1,1,1-Trifluoro-4-phenyl-3,4-epoxybutan-2-ol (9a). Method A. Compound **4a** (1.01 g, 5.0 mmol) in 15 mL of CH_2Cl_2 was placed into a one-necked flat-bottom flask, and a 85% solution of peracid **7** (1.08 g, 5.3 mmol) was added with stirring. When the starting compound disappeared (TLC monitoring with CH_2Cl_2 as the eluent), the reaction mixture was cooled to 0 °C, the precipitated *m*-chlorobenzoic acid was filtered off, and the residue was washed with a small amount of cooled CH_2Cl_2. The filtrate was washed with a solution of $NaHCO_3$ and with brine and dried with $MgSO_4$. Evaporation of the solvent gave 0.98 g (90 %) of a mixture of diastereomers **9a** as a light brown oil (TLC data). Found (%): C, 55.15; H, 4.18; F, 25.94. $C_{10}H_9F_3O_2$. Calculated (%): C, 55.05; H, 4.16; F, 26.12. IR, ν/cm^{-1}: 3360 (O—H).

Method B. Compound **4a** (1.01 g, 5.0 mmol), $VO(acac)_2$ (5 mg), and 20 mL of benzene were placed into a one-necked flat-bottom flask. Bu^{t}OOH (0.75 mL, 7.5 mmol) was added dropwise with stirring. When the starting compound disappeared (TLC monitoring), the reaction mixture was washed with a solution of $Na_2S_2O_5$ and water; the aqueous layer was extracted twice with ether, and the combined ether-benzene solution was dried with $MgSO_4$. Evaporation under reduced pressure with the temperature being maintained below 30 °C gave 0.97 g (89 %) of a mixture of diastereomers **9a** as a light yellow oil, practically identical to that prepared by method A. ^1H NMR ($CDCl_3$ + CD_3COOD), δ: 3.26—3.31 (m, 1 H, PhC<u>H</u>), 3.95 (d, 1 H, CH—O, J = 2.11 Hz), 4.11 (d, 1 H, CH—O, J = 2.11 Hz), 4.24 (m, 1 H, CF_3CH), 7.63 (m, 5 H, Ph) (the ratio between the diastereomers was 1:3).

4,4,5,5,6,6,6-Heptafluoro-1-phenyl-1,2-epoxyhexan-3-ol (9b). Method A. The reaction of **4b** (2.41 g, 7.98 mmol) with a 85% solution of peracid **7** (1.51 g, 8.77 mmol) according to the procedure described for **4a**, after stirring for 15 h and the subsequent workup, gave 2.40 g (94 %) of a mixture of diastereomers **9b** as a colorless thick oil (TLC data). Found (%): C, 45.11; H, 2.80; F, 41.91. $C_{12}H_9F_7O_2$. Calculated (%): C, 45.30; H, 2.85; F, 41.79.

Method B. The reaction of **4b** (1.55 g, 5.13 mmol), $VO(acac)_2$ (5 mg), and Bu^tOOH (0.77 mL, 7.7 mmol) according to the procedure described for **4a** gave 1.43 g (88 %) of a mixture of diastereomers **9b** as a colorless thick oil, practically identical to that prepared by method A. Column chromatography on SiO_2 (with $CHCl_3$ as the eluent) afforded one of the diastereomers of **9b** having the greater R_f in a pure state. ^1H NMR ($CDCl_3$), δ: 3.35 (s, 1 H, OH), 3.67 (m, 1 H, CH—O), 4.15 (d, 1 H, PhCH, J = 2.03 Hz), 4.49 (m, 1 H, C_3F_7CH); ^{13}C NMR ($CDCl_3$), δ: 68.00 (t, J = 23.96 Hz, CHOH), 58.51 (s, PhCH), 55.05 (s, CH—O). Based on these data, the signals corresponding to the diastereomer with the smaller R_f in the NMR spectrum of the mixture **9b** were assigned. ^1H NMR ($CDCl_3$), δ: 3.44 (t, 1 H, OH, J = 3.11 Hz), 3.67 (m, 1 H, CH—O), 3.92 (d, 1 H, PhCH, J = 2.11 Hz), 4.30 (m, 1 H, C_3F_7CH). The ratio between the diastereomers was 73:27. ^{13}C NMR ($CDCl_3$), δ: 55.22 (s, CH—O), 58.51 (s, PhCH), 68.53 (t, C_3F_7CH, J = 23.11 Hz).

Isomerization of 9a to 4,4,4-trifluoro-3-hydroxy-1-phenylbutan-2-one (10a). The benzene solution of the mixture of diastereomers **9a**, obtained by epoxidation of **4a** (3.5 g, 17.3 mmol) with Bu^tOOH (2.6 mL, 26.0 mmol) and $VO(acac)_2$ (17 mg) was concentrated at 70 °C under reduced pressure; during this process the color of the reaction mixture changed to dark brown. The residue was chromatographed on a column using $CHCl_3$ as the eluent to give 0.85 g (22 %) of compound **10a**, m.p. 74—75 °C (*cf.* Ref.[13]: m.p. 86 °C). Found (%): C, 55.66; H, 3.71; F, 25.77. $C_{10}H_9F_3O_2$. Calculated (%): C, 55.05; H, 4.16; F, 26.12. IR, ν/cm^{-1}: 3410, 3340 (OH), 1730 (C=O). ^1H NMR ($CDCl_3$), δ: 3.96 (d.d, J = 16.31 Hz, 2 H, CH_2), 4.59 (q, J = 7.51 Hz, 1 H, CF_3CH), 7.11—7.40 (m, 5 H, Ph).

1,1,1-Trifluoro-4-phenyl-3,4-epoxybutan-2-one (2a). Method A (oxidation with reagent **6**). The reaction of **9a** (1.35 g, 6.18 mmol), oxalyl chloride (0.69 mL, 8.03 mmol), DMSO (1.05 mL, 1.483 mmol), and NEt_3 (4.30 mL, 30.9 mmol) in 30 mL of anhydrous CH_2Cl_2, carried out according to the procedure described for compound **4a** followed by column chromatography, gave 0.22 g (15 %) of compound **11a** as colorless sticky crystals, m.p. 64—65 °C. IR, ν/cm^{-1}: 3370 (OH). ^1H NMR ($CDCl_3$ + CD_3COOD), δ: 3.43 (d, 1 H, CH—O, J = 1.76 Hz), 4.06 (d, 1 H, O—CH, J = 1.76 Hz), 7.33 (m, 5 H, Ph). The resulting compound was unstable during storage, and over a period of two or three days it was converted into a liquid, which, according to TLC (hexane—ethyl acetate, 3:1), was a complex mixture of products.

Method B (oxidation with reagent **5**). The reaction of **9a** (1.09 g, 5.0 mmol) and **5** (2.76 g, 6.5 mmol) in 40 mL of anhydrous CH_2Cl_2, according to the procedure described for compound **4a**, gave 1.04 g (89 %) of compound **11a**, which was identical to the sample prepared by method A, according to its IR and ^1H NMR spectra.

4,4,5,5,6,6,6-Heptafluoro-1-phenyl-1,2-epoxyhexan-3-one (2b). Method A (oxidation with reagent **6**). The reaction of **9b** (2.40 g, 7.54 mmol), oxalyl chloride (0.84 mL, 9.84 mmol), DMSO (1.34 mL, 18.85 mmol), and NEt_3 (5.24 mL, 37.7 mmol) in 35 mL of anhydrous CH_2Cl_2, carried out according to the procedure described for compound **9a** followed by column chromatography (with $CHCl_3$—ether, 5:1, as the eluent), gave 1.64 g (65 %) of a light brown oil that crystallized very slowly. Found (%): C, 43.40; H, 2.81; F, 39.59. $C_{12}H_9F_7O_3$ (monohydrate **11b**). Calculated (%): C, 43.13; H, 2.72; F, 39.79. IR, ν/cm^{-1}: 3400 (OH), 1760 (C=O). The compound obtained was unstable during storage and was converted into a liquid consisting of a complex mixture of products (TLC data) over a period of one week.

Method B (oxidation with reagent **5**). The reaction of **9b** (0.172 g, 0.541 mmol) and reagent **5** (0.298 g, 0.703 mmol) in 10 mL of anhydrous CH_2Cl_2, according to the procedure described for compound **9a**, gave 0.160 g (91 %) of monohydrate **11b** with a minor admixture of free ketone **2b**; the IR spectrum of the product was identical to that of the compound obtained with reagent **6**.

2-(1',2'-Epoxyethyl-2'-phenyl)-2-trifluoromethyl-1,3-dioxolane (12a). Potassium carbonate (0.1 g) and 2-chloroethanol (1 mL) was added to compound **11a** (0.100 g, 0.427 mmol). The reaction mixture was stirred at ~20 °C until the starting **11a** disappeared (TLC monitoring, hexane—ethyl acetate, 3:1, as the eluent) and then treated with 5 mL of CH_2Cl_2 and 3 mL of water. The organic layer was separated, and the aqueous layer was extracted with ether (3×3 mL). The combined extract was washed with water and brine and filtered through a SiO_2 layer, and the filtrate was concentrated to give 0.059 g (53 %) of compound **12a** as a colorless oil that was pure according to TLC and ^1H NMR spectroscopy. IR, ν/cm^{-1}: no νOH or νCO bands. ^1H NMR ($CDCl_3$), δ: 3.36 (m, 1 H, CH—O), 4.02 (d, 1 H, CH—O, J = 2.11 Hz), 4.14 (m, 4 H, OCH_2CH_2O), 7.31 (m, 5 H, Ph).

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