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Perfluoroalkyl Migration in the Rearrangement of 4-Perfluoroalkyl-4-quinols

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Abstract: Heating a DMSO solution of 4-(perfluoro-*n*-alkyl)-4-hydroxy-2,5-cyclohexadien-1-one (4-perfluoroalkyl-4-quinols) in the presence of a catalytic amount of base brought about 1,2-migration of the perfluoroalkyl group to give 2-(perfluoro-*n*-alkyl)hydroquinone or 5-(perfluoro-*n*-alkyl)-2-cyclohexene-1,4-dione depending upon the substitution pattern of the quinol. The similar rearrangement of 4-perfluoroisopropyl-4-hydroxy-2,5-cyclohexadien-1-one occurred very smoothly at room temperature under the basic conditions. 5-Hydroxy-4-methyl-5-perfluorooctyl-1-propyl-3-pyrrolin-2-one underwent the base-induced rearrangement to afford a perfluorooctylated succinimide derivative. On the other hand, 5-hydroxy-3-methyl-5-perfluorooctyl-1-propyl-3-pyrrolin-2-one and 5-hydroxy-1-isobutyl-5-perfluorooctyl-3-pyrrolin-2-one did not suffer any rearrangement, although their structures were very similar to the 4-methylated one.

Many rearrangement reactions of 4-hydroxy-2,5-cyclohexadien-1-ones (4-quinols) and their derivatives have been recorded in the literature. For example, acid-catalyzed rearrangement of 4-substituted 4-quinols in a protic solvent or acetic anhydride giving hydroquinones or resorcinol diacetates is known as the quinol rearrangement (the dienone-phenol rearrangement).[1] Base-catalyzed reaction of 4-quinols giving hydroquinones is known as the acyloin rearrangement.[2] Photo-induced ring contraction of 4-quinols to 2-cyclopentenones is considered as a variant of the di-π-methane rearrangement (the Zimmermann rearrangement).[3]

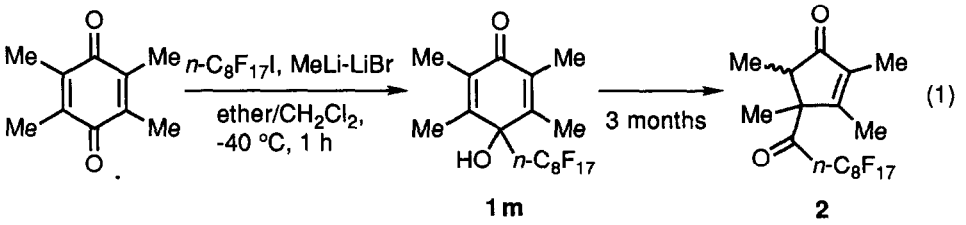
During our continuing studies on the syntheses and reactions of perfluoroalkyl-containing compounds, anomalous 1,3-migration of an acetoxyl group was revealed during the acid treatment of 4-perfluoroalkyl-4-quinols in acetic anhydride.[4] The rearrangement can be regarded as a typical example of the effect of a strongly electron withdrawing perfluoroalkyl group on cationic intermediates. This finding encouraged us to investigate other rearrangements of 4-perfluoroalkyl-4-quinols and led to the first discovery of perfluoroalkyl migration under basic conditions.[5] However, the applicability of this acyloin type migration of perfluoroalkyl groups was severely limited. In this paper, we wish to describe full details of our study on the unique 1,2-shift of perfluoroalkyl groups under base-catalyzed conditions.

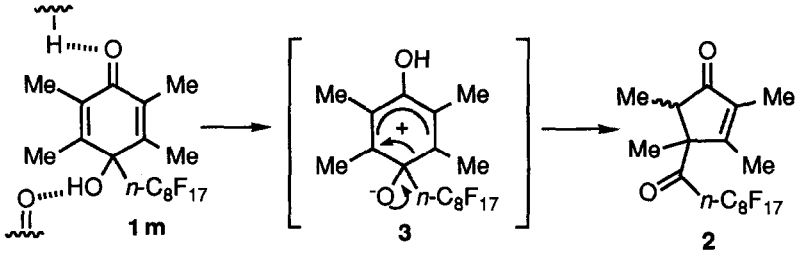
RESULTS AND DISCUSSION

Preparation of 4-perfluoroalkyl-4-quinols **1**

4-Perfluoroalkyl-4-quinols were prepared by the reaction of quinones with perfluoroalkyllithium generated *in situ* by the previously reported method.[4] Some of them were worthy of mention. Perfluorooctylation of duroquinone occurred under the usual conditions to give the desired quinol **1m** as color-

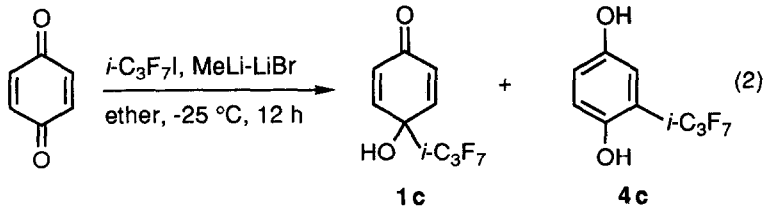
less fine needles in a 52% yield (Eq 1). After the quinol **1m** was stored in a dark cupboard for about 3 months, it became a colorless sticky mass, GC-MS analysis of which revealed the presence of a new compound with the same molecular composition in ca. 30% yield. Chromatographic purification of the material gave a colorless oil in the less polar fractions and quinol **1m** in the polar fractions. This less polar compound was assigned as 2-cyclopentenone **2** on the basis of ^{1}H NMR, ^{13}C NMR, and IR spectra. This reaction may be regarded as an acyloin ring contraction[6] or the Zimmermann rearrangement.[7] Our tentative explanation for the ring contraction illustrated in Scheme 1 involves initial intermolecular protonation to give a betaine **3**, but a precise discussion is beyond the scope of this paper.

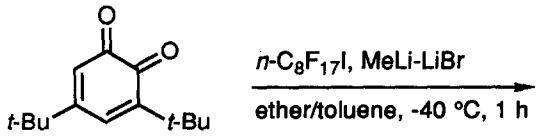


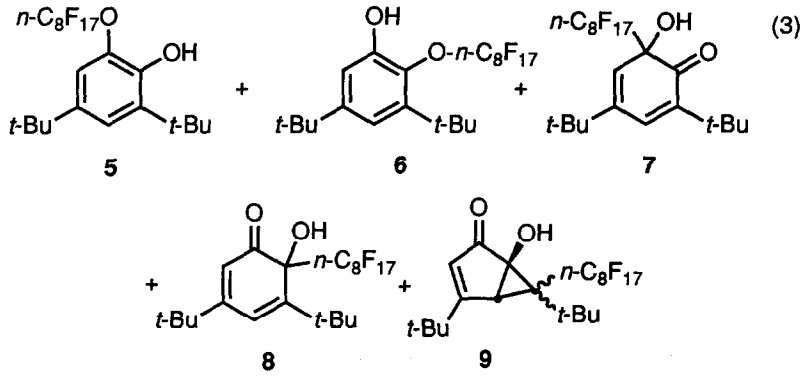


Scheme 1. Possible Reaction Route to **2**

The reaction of 1,4-benzoquinone with perfluoroisopropyl iodide did not take place under the usual conditions but gave a mixture of quinol **1c** (22%) and hydroquinone **4c** (14%) after 12 h at -25 °C (Eq 2). Perfluoroalkylation of *o*-quinones gave very complex results. For example, perfluorooctylation of 3,5-di-*t*-butyl-1,2-benzoquinone under the usual conditions gave a complex mixture, from which five perfluorooctylated isomers were obtained in 56% combined yield: catechol perfluorooctyl ethers **5** (28%) and **6** (18%), quinols **7** and **8**, and an unassigned compound **9** (**7**:**8**:**9** = 3:2:5, 10%) (Eq 3). The compound **9** was tentatively thought to have a bicyclo[3.1.0]hexenone skeleton by the diagnosis of its spectroscopic data (see experimental). Interestingly, when the compound **9** was left in solution for 1 day, it partially isomerized to form a mixture (1:1) of **9** and an isomer, the latter presumably being epimeric with **9** at the carbon bearing perfluorooctyl and *t*-butyl groups.

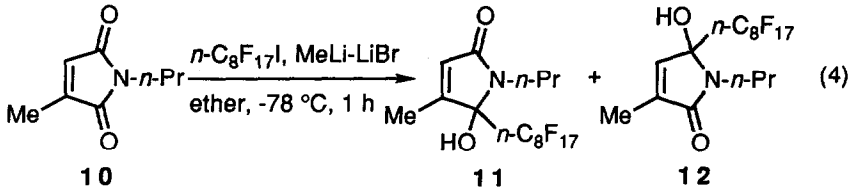






(3)

Perfluorooctylation of citraconimide **10** was carried out according to the reported method[8] to give a mixture of **11** and **12** in respective yields of 61% and 26% (Eq 4). A similar preference for attack at the more hindered carbonyl group has been reported in the reduction of citraconic anhydride.[9]

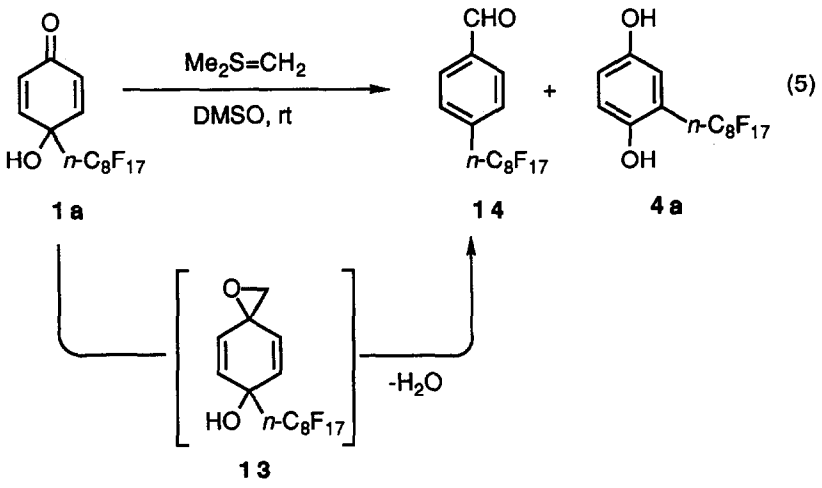


(4)

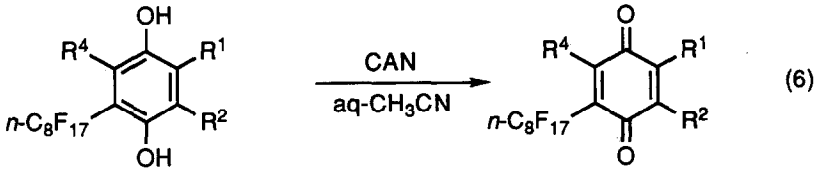
Attempted preparation of 4-(perfluoroalkyl)benzaldehydes

Initially, we intended to prepare *p*-(perfluorooctyl)benzaldehyde, which would be a useful synthetic precursor for perfluoroalkyl-containing aromatic compounds, via the rearrangement of 6-hydroxy-6-perfluorooctyl-1-oxaspiro[2.5]octa-4,7-diene (**13**). In order to prepare the spiro compound, 4-perfluorooctyl-4-quinol (**1a**) was treated with 5 equiv of dimethylsulfonium methylide in DMSO for 2 h at room temperature (Eq 5). The main products were, however, (perfluorooctyl)benzenediol (64%) and 4-(perfluorooctyl)benzaldehyde (**14**; 7%). The benzenediol was unambiguously identified as 2-(perfluorooctyl)hydroquinone (**4a**) by diagnosis of spectroscopic data as well as by quantitative transformation to 2-perfluorooctyl-1,4-benzoquinone (**15a**; Eq 6, $R^1 = R^2 = R^4 = H$) by ceric ammonium nitrate (CAN). Changing the reagent to dimethyloxosulfonium methylide resulted in the formation of a complex mixture, from which the hydroquinone **4a** was

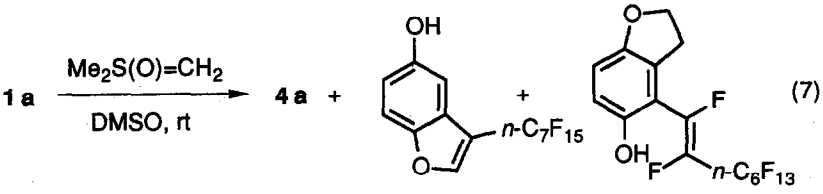
isolated in a 21% yield along with other perfluoroalkyl-containing compounds **16** (5%) and **17** (3%) (Eq 7). The rather unexpected furan structures **16** and **17** were assigned from their NMR data (see experimental). Their formation may be rationalized by the elimination of fluoride anions from **18** leading to *o*-quinomethide intermediates **19** and **23** followed by the addition of dimethyloxosulfonium methylide (Scheme 2).



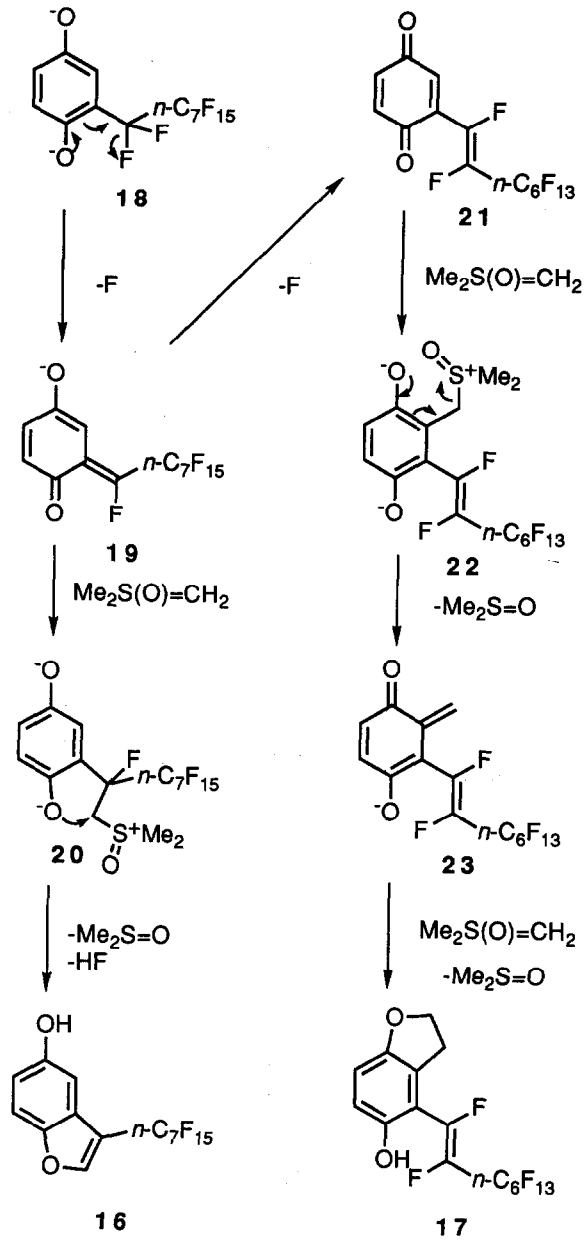
1a **14** **4a** **13** (5)



4 **15** (6)



16 **17** (7)



Scheme 2. Proposed Formation Routes to **16** and **17**

The Acyloin Rearrangement of 4-Perfluoroalkyl-4-quinols 1

We turned our attention to the formation of hydroquinone **4a**. This reaction is regarded as the acyloin rearrangement involving 1,2-migration of the perfluorooctyl group. To our knowledge, the migration of a perfluoroalkyl group is not known under either acidic or basic conditions. The strongly electronegative character of the perfluoroalkyl group suppresses its migration toward an electrophilic center, while easy elimination of fluoride anion again prevents the migration of the perfluoroalkyl anionic species. Thus, we decided to investigate the rearrangement in detail.

First, the rearrangement of **1a** to **4a** was examined under various conditions in order to optimize the yields (Table 1). Potassium *t*-butoxide, sodium methylsulfinylmethanide derived from sodium hydride and DMSO, and spray-dried KF[10] were all effective as the base, although the latter two bases were somewhat inferior to the first one. At room temperature, the rearrangement proceeded slowly (entry 6) and more than 1 equiv of the base was required for the complete disappearance of **1a**, whereas at 80 °C **1a** almost disappeared within 3 h even with a catalytic amount of bases (entries 1, 4, and 7). In a polar aprotic solvent such as DMSO, DMF, HMPA, and sulfolane, the rearrangement proceeded smoothly (entries 6-10), while in diglyme, THF, dioxane, and *t*-butanol results were poor: none of the desired product was obtained in the latter three solvents (entries 12-14) and only partial conversion to **4a** was observed in diglyme (entry 11). In the cases where the rearrangement took place, a small amount of 1,4-bis(perfluorooctyl)-2,5-cyclohexadiene-1,4-diol (**24**) was formed (<5%) along with a variable amount of tarry material.

Table 1. The Acyloin Rearrangement of **1a** to **4a**

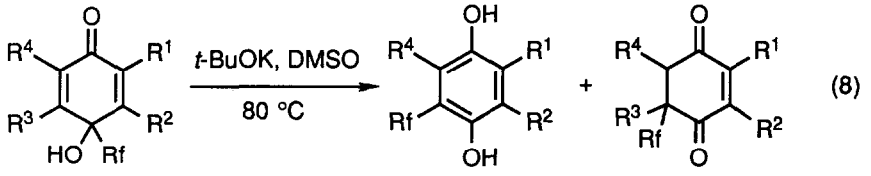
Entry	Base	Equiv	Solvent	Temp/°C	Time/h	Yield/%[a]	
						1a	**4a**
1	NaH	0.1	DMSO	80	11	4	69
2	NaH	5.0	DMSO	rt	3	-	64
3	KF	5.0	DMSO	80	3	-	20[b]
4	KF	0.1	DMSO	80	3	trace	79[b]
5	*t*-BuOK	1.0	DMSO	rt	168	trace	60
6	*t*-BuOK	0.1	DMSO	rt	144	30	39
7	*t*-BuOK	0.1	DMSO	80	3	-	81
8	*t*-BuOK	0.1	DMF	80	2	-	77
9	*t*-BuOK	0.1	HMPA	80	2	-	63
10	*t*-BuOK	0.1	sulfolane	80	3	-	70
11	*t*-BuOK	0.1	diglyme	80	24	30	12
12	*t*-BuOK	0.1	THF	reflux	24	57	-
13	*t*-BuOK	0.1	dioxane	80	24	76	-
14	*t*-BuOK	0.1	*t*-BuOH	60	7	57	-

[a] Isolated yield. [b] Compound **24** was obtained in 5 % yield.

Next, a variety of 4-perfluoroalkyl-4-quinols were subjected to the acyloin rearrangement using the conditions which gave the highest yields of **4a** (entry 7 in Table 1) and the results obtained are listed in Table 2 (Eq 8). Contrary to perfluoro-*n*-alkyl groups, the migration of a perfluoroisopropyl group occurred very smoothly. The quinol **1c** disappeared within 10 min even at room temperature to give the corresponding hydroquinone **4c** in a 76% yield. It is worth noting that neither the same hydroquinone nor the same cyclo-

hexenedione was obtained in the rearrangement of regioisomeric quinols derived from the perfluorooctylation of the same quinone (entries 3 *vs* 4 and 5 *vs* 6). A *t*-butyl group retarded the rearrangement even in the case of 2-*t*-butyl-4-perfluorooctyl-4-quinol (**1i**), where the perfluorooctyl group moved to the *para* position against the *t*-butyl group (entry 8). The rearrangement of quinol **1m** derived from duroquinone took place to afford a diastereomeric mixture of cyclohexenedione **25m** (*E*:*Z* = 4:5) in a 40% yield along with duroquinone (31%) and duroquinone dimer[11] (21%) (entry 12). Stereochemical assignment of **25m** was based on the "through-space" long-range coupling[12] between vicinal methyl and perfluorooctyl groups:[13] only the *cis* isomer of **25m** showed such coupling (J = 3.4 Hz, see experimental). The compound **25m** was rather unstable and gradually decomposed to duroquinone in solution at room temperature. Quinols **1j**, **1k**, and **1l** did not undergo the rearrangement but suffered partial decomposition on prolonged standing (entries 9-11).

Table 2. The Acyloin Rearrangement of Various Quinols **1**



1 **4** **25**

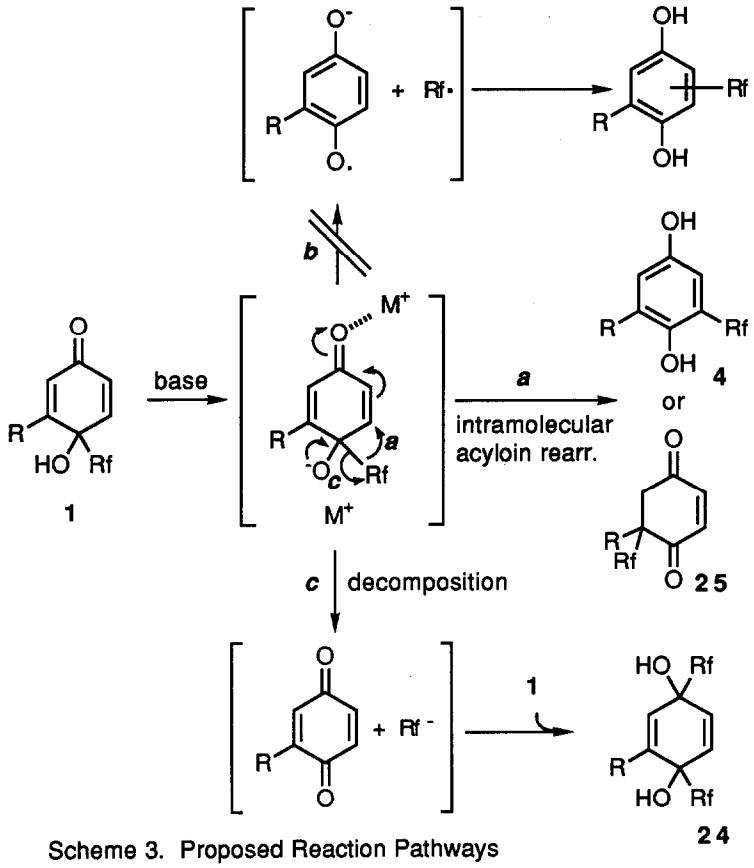
Entry	Quinol						Time/h	Yield/%[a]		
	1	R^1	R^2	R^3	R^4	Rf		**1**	**4**	**25**
1	**b**	H	H	H	H	*n*-C_6F_{13}	3	-	64	-
2	**c**	H	H	H	H	*i*-C_3F_7	0.2[b]	-	76	-
3	**d**	Me	H	H	H	*n*-C_8F_{17}	3	-	47	-
4	**e**	H	Me	H	H	*n*-C_8F_{17}	0.5	-	46	trace[c]
5	**f**	Me	H	H	Me	*n*-C_8F_{17}	24	40	4	-
6	**g**	H	Me	Me	H	*n*-C_8F_{17}	0.5	-	-	66
7	**h**	Me	H	Me	H	*n*-C_8F_{17}	0.5	-	-	35
8	**i**	*t*-Bu	H	H	H	*n*-C_8F_{17}	24	62	23	-
9	**j**	*t*-Bu	H	H	*t*-Bu	*n*-C_8F_{17}	24	53	-	-
10	**k**	H	OMe	H	H	*n*-C_4F_9	24	58	-	-
11	**l**	-CH=CH-CH=CH-		H	H	*n*-C_6F_{13}	6	64	-	-
12	**m**	Me	Me	Me	Me	*n*-C_8F_{17}	1	-	-	40[d]

[a] Isolated yield. [b] The reaction was carried out at room temperature. [c] 5-Methyl-5-perfluoro-octyl-2-cyclohexene-1,4-dione (**25e'**) was obtained. [d] Diastereomer mixture (*E*:*Z*= 4:5). Duroquinone and its dimer were obtained in 31 % and 21 % yields.

Reaction Mechanism Consideration

Two possible routes are thought for the rearrangement of quinol **1** to **4** or **25**: **a**) the intramolecular rearrangement of perfluoroalkyl anionic species to an adjacent electrophilic carbon and **b**) the dissociation of the quinol anion into a quinone anion radical and a perfluoroalkyl radical followed by recombination of these radicals (Scheme 3). In order to obtain a closer insight into the mechanism, two additional experiments were

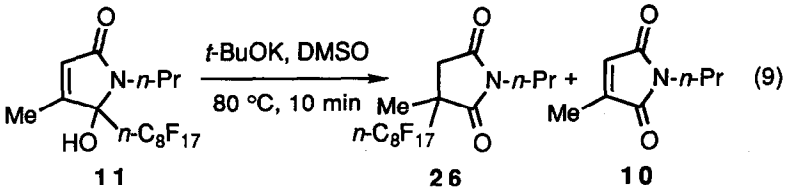
carried out. A mixture of **1b** and **1d** (1:1) was treated under the usual conditions (DMSO, 80 °C, 3 h). No formation of a cross-over product was detected, however, by GC-MS analysis of the reaction mixture. When quinol **1a** was heated with 5 equiv of 2,5-dimethyl-1,4-benzoquinone in the presence of potassium *t*-butoxide (0.1 equiv), GC-MS analysis of the reaction mixture revealed the existence of **25h** in a small amount in addition to **4a**. From these results and the strict regiospecificity mentioned above, the mechanistic pathway from **1** to **4** or **25** is thought to be an intramolecular vinylogous acyloin rearrangement (path **a** in Scheme 3): decomposition of the intermediate quinol anion into the parent quinone and a perfluoroalkyl anionic species plays a role in by-product formation (path **c**).

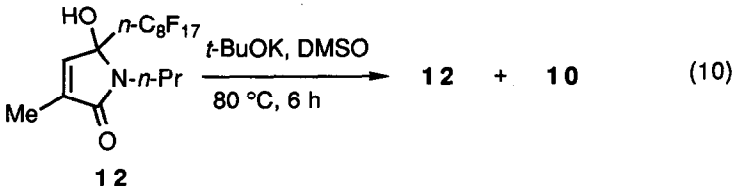


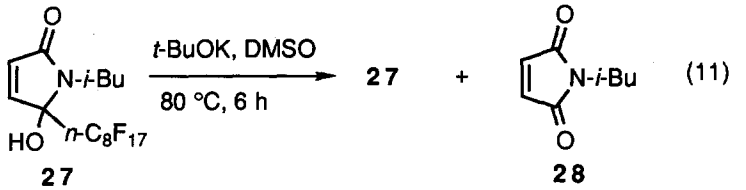
Scheme 3. Proposed Reaction Pathways

Other Related Acyloin Rearrangement

In order to extend the perfluoroalkyl migration reaction, we investigated the reaction using perfluoroalkylated enamides,[14] skeleton of which was in part similar to the quinol **1**. Brief heating (5 min) of **11** at 80 °C in DMSO in the presence of potassium *t*-butoxide (0.1 equiv) gave the perfluoroalkyl migration product **26** in 41 % yield as well as the parent citraconimide (**10**; 20%) (Eq 9). The rearrangement of enamides **12** and **27**,[8] however, did not take place and prolonged heating of them simply brought about decomposition into the parent imides **10** and **28** (Eqs 10 and 11).







Summary

We have shown the first example of perfluoroalkyl migration under basic conditions, which may be regarded as the vinylogous acyloin rearrangement. In the rearrangement a tendency has been observed that the presence of a substituent next to the carbonyl group in quinol or 3-pyrrolin-2-one retards the migration, whereas the presence of substituent groups adjacent to the perfluoroalkyl group promotes the rearrangement. Further study to investigate other examples of perfluoroalkyl rearrangements is under way.

Acknowledgement

This work has been supported by a Grant-in-Aid for Scientific Research No. 02750619 from the Ministry of Education, Science and Culture. We thank Dr. Kazuhiro Shimokawa (Daikin Kogyo Co. Ltd.) for a generous gift of perfluoroalkyl iodides.

EXPERIMENTAL

Melting points are uncorrected. Distillation was carried out by using a Kugelrohr apparatus. Unless otherwise specified, NMR spectra were obtained with a GSX-270 spectrometer at ambient temperature by using $CDCl_3$ as the solvent, tetramethylsilane as an internal standard for ^1H and ^{13}C, and $CFCl_3$ for ^{19}F. Mass spectra were measured with a Hitachi M80B-LCAPI spectrometer under the following ionizing conditions: EI (electron impact, 20 eV) and CI (chemical ionization, 70 eV, methane as CI gas). Column chromatography was carried out using Wakogel C-200. Gas liquid chromatography was run using a Shimadzu GC-14A apparatus with a 3% OV-1 packed column (1 m) and/or a CBP10-M25 capillary column (25 m). Preparative GPC was performed using a JAI LC-08 apparatus with JAI-1H (20 mmID x 60 cm) and JAI-2H (20 mmID x 60 cm) columns. Ether and THF were distiled from sodium benzophenone ketyl. Diglyme and dioxane were distiled from sodium under an argon atmosphere. Dichloromethane, HMPA, and toluene were distiled from CaH_2 under an argon atmosphere. Sulfolane was distiled under an argon atmo-

sphere and stored over 4 Å molecular sieves. Methyllithium-lithium bromide was prepared from lithium and methyl bromide in ether as usual. Other commercially available materials were used without further purification.

*4-Hydroxy-2,3,5,6-tetramethyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (**1m**).* To a solution of duroquinone (0.657 g, 4 mmol) and *n*-$C_8F_{17}I$ (2.621 g, 4.8 mmol) in ether (40 ml) and CH_2Cl_2 (20 ml) was slowly added an ethereal solution of MeLi-LiBr (1.1 mol l^{-1}: 4 ml, 4.4 mmol) at -40 °C. The mixture was stirred for 1 h at -40 °C and then quenched with aq NH_4Cl. The organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2/ether) to give 1.210 g (52%) of **1m** as colorless needles; mp 94-95 °C (CH_2Cl_2/hexane). ^1H NMR δ = 1.92 (6H, br s), 2.09 (6H, br s), and 3.07 (1H, s); ^{13}C NMR δ = 11.95, 15.48 (t, *J* = 4 Hz), 75.01 (t, *J* = 20 Hz), 105-125 (8C), 135.64, 145.36, and 182.32; ^{19}F NMR δ = -81.27 (3F, tt, *J* = 10 and 3 Hz), -112.68 (2F, m), -121.02 (2F, m), -121.80 (2F, m), -122.35 (4F, m), -123.25 (2F, m), and -126.66 (2F, m); IR (KBr) 3352s, 1670s, 1630vs, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 584 (M^+, 1), 555 (0.3), 165 (100), and 137 (20). Anal Calcd for $C_{18}H_{13}F_{17}O_2$: C, 37.00; H, 2.24%. Found: C, 36.98; H, 2.39%.

*2,3,4,5-Tetramethyl-4-perfluorononanoyl-2-cyclopenten-1-one (**2**).* Colorless oil (3:2 diastereomer mixture); ^1H NMR δ = 1.10 (3H of major isomer, d, *J* = 7.6 Hz), 1.18 (3H of minor isomer, d, *J* = 7.3 Hz), 1.36 (3H of minor isomer, s), 1.59 (3H of major isomer, d, *J* = 1.8 Hz), 1.78 (both 3H, s), 1.95 (3H of major isomer, s), 1.99 (3H of minor isomer, s), 2.44 (1H of major isomer, q, *J* = 7.6 Hz), and 2.70 (1H of minor isomer, q, *J* = 7.3 Hz); ^{13}C NMR (major isomer) δ = 8.49, 11.30 (t, *J* = 1 Hz), 13.49, 13.49, 16.97, 20.86, 52.92. 62.21 (m), 105-125 (8C), 138.28, 165.66, 195.04 (t, *J* = 26 Hz), and 206.62; (minor isomer) δ = 8.38, 10.68, 13.78, 16.97, 20.91, 45.84 (d, *J* = 3 Hz), 60.78 (m), 105-125 (8C), 136.74, 167.22, 195.28 (t, *J* = 25 Hz), and 206.67; ^{19}F NMR δ = -81.26 (both 3F, t, *J* = 10 Hz), -112.17 (1F of minor isomer, dtm, *J* = 302 and 14 Hz), -112.68 (1F of major isomer, dtm, *J* = 312 and 14 Hz), -115.16 (1F of minor isomer, dtm, *J* = 302 and 14 Hz), -115.56 (1F of major isomer, dtm, *J* = 312 and 14 Hz), -120.81 (2F of major isomer, m), -121.07 (2F of minor isomer, m), -121.55 (both 2F, m), -122.33 (both 4F, m), -123.21 (both 2F, m), and -126.61 (both 2F, m); IR (neat) 2984m, 1740vs, 1714vs, 1658s, and 1300-1100vs cm^{-1}; MS (CI) *m/z* (rel intensity) 585 (M^++1, 43), 565 (4), 545 (3), 137 (100), and 109 (42). HRMS Found: *m/z* 584.0669. Calcd for $C_{18}H_{13}F_{17}O_2$: M, 584.0643.

*4-Hydroxy-4-perfluoroisopropyl-2,5-cyclohexadien-1-one (**1c**).* To a solution of benzoquinone (1.081 g, 10 mmol) and *i*-C_3F_7I (3.551 g, 12 mmol) in ether (100 ml) was slowly added an ethereal solution of MeLi-LiBr (11 mmol) at -25 °C. The mixture was kept in a freezer (-25 °C) overnight. An aq solution of NH_4Cl was added to the mixture. The organic phase was separated and the aqueous phase was extracted with ether (3 x 20 ml). The combined ethereal extract was washed with brine, dried over Na_2SO_4, and concentrated. Chromatography of the residue on silica gel (CH_2Cl_2/ether) gave 0.612 g (22%) of the quinol **1c** and 0.528 g (19%) of hydroquinone **4c**. **1c**: colorless needles, mp 86-87 °C (CH_2Cl_2/hexane). ^1H NMR δ = 4.09 (1H, s), 6.35 (2H, d, *J* = 10.4 Hz), and 7.04 (2H, d, *J* = 10.4 Hz); ^{13}C NMR δ = 69.98 (d, *J* = 22 Hz), 93.96 (d-septet, *J* = 247 and 30 Hz), 120.24 (dq, *J* = 290 and 26 Hz), 130.34, 141.79, and 184.15; ^{19}F NMR δ = -71.27 (6F, d, *J* = 6 Hz) and -183.01 (1F, septet, *J* = 6 Hz); IR (KBr) 3220vs, 1678vs, 1628vs, 1406s, 1388s, and 1300-1100vs cm^{-1}; MS (CI) *m/z* (rel intensity) 279 (M^++1, 28), 261 (18), 151 (8), 138 (17), 110 (100), and 109 (44). Anal Calcd for $C_9H_5F_7O_2$: C, 38.87; H, 1.81%. Found: C, 38.97; H, 1.90%.

Perfluorooctylation of 3,5-Di-t-butyl-1,2-benzoquinone

The reaction of 3,5-di-*t*-butyl-1,2-benzoquinone (0.881 g, 4 mmol) with *n*-$C_8F_{17}I$ (2.621 g, 4.8 mmol) was carried out according to the procedure described for **1m**. The residue was chromatographed on silica gel to

give 0.717 g (28%) of **5**, 0.460 g (18%) of **6**, 0.278 g of a mixture of **7**, **8**, and **9** (**7**:**8**:**9**: = 3:2:5). Separation of **9** from the mixture was performed by using preparative GPC. 2,4-Di-*t*-butyl-6-(perfluorooctyloxy)phenol (**5**): colorless crystals, mp 44-45 °C (CH_2Cl_2/hexane); ^1H NMR δ = 1.29 (9H, s), 1.42 (9H, s), 5.24 (1H, s), 7.10 (1H, m), and 7.25 (1H, d, *J* = 2.4 Hz); ^{13}C NMR δ = 29.39, 31.38, 34.47, 35.31, 105-125 (8C), 116.24, 122.36, 135.68, 137.53, 142.68, and 144.07; ^{19}F NMR δ = -81.30 (3F, tt, *J* = 10 and 2 Hz), -83.00 (2F, m), -122.18 (6F, m), -123.17 (2F, m), -125.17 (2F, m), and -126.57 (2F, m); IR (KBr) 3600s, 2956s, 1592m, 1486s, 1416s, 1340s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 641 (M^++1, 8), 640 (M^+, 28), 625 (100), 605 (9), and 69 (6). Anal Calcd for $C_{22}H_{21}F_{17}O_2$: C, 41.26; H, 3.31%. Found: C, 41.38; H, 3.31%. 3,5-Di-*t*-butyl-2-(perfluorooctyloxy)phenol (**6**): colorless crystals, mp 37-38 °C (CH_2Cl_2/hexane); ^1H NMR δ = 1.29 (9H, s), 1.39 (9H, s), 5.14 (1H, br s), 6.89 (1H, d, *J* = 2.4 Hz), and 7.06 (1H, d, *J* = 2.4 Hz); ^{13}C NMR δ = 31.17, 31.62, 34.71, 36.11, 105-125 (8C), 112.81, 118.25, 132.07, 143.95, 148.59 and 150.68; ^{19}F NMR δ = -78.95 (2F, t, *J* = 10 Hz), -81.28 (3F, tt, *J* = 10 and 2 Hz), -122.02 (2F, m), -122.25 (4F, m), -123.15 (2F, m), -123.82 (2F, m), and -126.60 (2F, m); IR (KBr) 3636s, 3384s, 2968vs, 1590s, 1424s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 641 (M^++1, 13), 640 (M^+, 51), 625 (79), 605 (34), 585 (6), and 57 (100). Anal Calcd for $C_{22}H_{21}F_{17}O_2$: C, 41.26; H, 3.31%. Found: C, 40.99; H, 3.17%. 2,4-Di-*t*-butyl-6-hydroxy-6-perfluorooctyl-2,4-cyclohexadien-1-one (**7**): ^1H NMR δ = 1.06 (9H, s), 1.50 (9H, s), 5.86 (1H, d, *J* = 2.4 Hz), and 6.74 (1H, d, *J* = 2.4 Hz) (OH was not seen). 3,5-Di-*t*-butyl-6-hydroxy-6-perfluorooctyl-2,4-cyclohexadien-1-one (**8**): ^1H NMR δ = 1.28 (9H, s), 1.44 (9H, s), 5.95 (1H, s), 7.11 (1H, d, *J* = 2.4 Hz), and 7.34 (1H, d, *J* = 2.4 Hz). 4,6-Di-*t*-butyl-1-hydroxy-6-(perfluorooctyl)bicyclo[3.1.0]hex-3-en-2-one (**9**) (tentative assignment): colorless crystals, mp 134-135 °C (CH_2Cl_2/hexane); ^1H NMR (acetone-d_6) δ = 0.98 (9H, s), 1.17 (9H, s), 3.77 (1H, br s), 7.20 (1H, s), and 7.43 (1H, br s); ^{13}C NMR (acetone-d_6) δ = 26.47, 28.84, 33.42, 37.05, 65.47, 98.79, 105-125 (8C), 107.14 (t, *J* = 28 Hz), 150.15, 158.36, and 197.96; ^{19}F NMR (acetone-d_6) δ = -80.64 (3F, t, *J* = 10 Hz), -117.07 (1F, dm, *J* = 310 Hz), -119.92 (1F, dm, *J* = 291 Hz), -121.33 (6F, m), -122.26 (2F, m), and -125.75 (2F, m); IR (KBr) 3456vs, 2964s, 1720vs, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 640 (M^+, 5), 625 (13), 605 (3), 600 (4), 231 (9), 181 (15), 154 (49), 131 (100), and 69 (53). Isomer of **9**: ^1H NMR (acetone-d_6) δ = 1.01 (9H, s), 1.16 (9H, s), 3.55 (1H, br s), 7.19 (1H, s), and 7.44 (1H, br s); ^{13}C NMR (acetone-d_6) (typical signals) δ = 26.92, 28.75, 33.28, 36.24, 70.26 (d, *J* = 2 Hz), 97.85, 116.26 (t, *J* = 30 Hz), 151.30, 158.38, and 199.14 (m); ^{19}F NMR (acetone-d_6) (typical signals) δ = -114.12 (1F, dm, J = 288 Hz) and -115.42 (1F, dm, J = 288 Hz).

*5-Hydroxy-4-methyl-5-perfluorooctyl-1-propyl-3-pyrrolin-2-one (**11**) and 5-Hydroxy-3-methyl-5-perfluorooctyl-1-propyl-3-pyrrolin-2-one (**12**).* Perfluorooctylation of imide **10** (1.532 g, 10 mmol) was carried out by the reported procedure[8] to give 3.497 g (61%) of **11** and 1.490 g (26%) of **12**. **11**: colorless crystals, mp 93-94 °C (CH_2Cl_2/hexane); ^1H NMR δ = 0.91 (3H, t, *J* = 7.3 Hz), 1.67 (2H, m), 2.08 (3H, d, *J* = 1.5 Hz), 3.16 (1H, m), 3.51 (1H, m), 3.74 (1H, s), and 5.95 (1H, q, *J* = 1.5 Hz); ^{19}F NMR δ = -81.31 (3F, tt, *J* = 10 and 2 Hz), -112.71 (1F, dm, *J* = 307 Hz), -118.94 (1F, dm, *J* = 307 Hz), -120.27 (1F, dm, *J* = 307 Hz), -121.8--122.4 (7F, m), -123.13 (2F, m), and -126.51 (2F, m); IR (KBr) 3200vs, 2972s, 1684vs, 1656vs, 1372s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 573 (M^+, 3), 544 (26), 515 (7), 487 (1), 154 (100), and 112 (29). Anal Calcd for $C_{16}H_{12}F_{17}NO_2$: C, 33.52; H, 2.11; N, 2.44%. Found: C, 33.92; H, 2.22; N, 2.56%. **12**: colorless crystals, mp 91-92 °C (CH_2Cl_2/hexane); ^1H NMR δ = 0.92 (3H, t, *J* = 7.3 Hz), 1.72 (2H, m), 1.94 (3H, d, *J* = 1.5 Hz), 3.12 (1H, d, *J* = 1.5 Hz), 3.27 (1H, m), 3.47 (1H, m), and 6.58 (1H, m); ^{19}F NMR δ = -81.25 (3F, tt, *J* = 10 and 2 Hz), -119.00 (1F, dm, *J* = 279 Hz), -119.80 (1F, dm, *J* = 294 Hz), -120.0 (1F, dm, *J* = 279 Hz), -121.1 (1F, dm, *J* = 294 Hz), -122.25 (6F, m), -123.14 (2F, m), and -126.58 (2F, m); IR (KBr) 3188vs, 1686vs, 1372s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 573 (M^+, 1), 544 (21), 515 (12), 487 (1), 459 (1), 154 (100), and 112 (18).

Reaction of 1a with Dimethylsulfonium Methylide

To a solution of dimethylsulfonium methylide[15] (20 mmol) in DMSO (10 ml) was added a solution of quinol **1a** (2.112 g, 4 mmol) in DMSO at 5-10 °C. The mixture was stirred for 2 h at room temperature and aq NH_4Cl was added. The mixture was extracted with ether (3 x 30 ml). The ethereal extract was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2/ether) to give 0.147 g of 4-(perfluorooctyl)benzaldehyde (**14**) and 1.352 g of **4a**. **14**: colorless needles, mp 157-158 °C (CH_2Cl_2/hexane); ^1H NMR δ = 7.79 (2H, d, *J* = 8.2 Hz), 8.03 (2H, d, *J* = 8.2 Hz), and 10.12 (1H, s); ^{13}C NMR δ = 105-125 (8C), 127.76 (t, *J* = 6 Hz), 129.66, 134.29 (t, *J* = 24 Hz), 138.74 (t, *J* = 1 Hz), and 191.09; ^{19}F NMR δ = -81.29 (3F, t, *J* = 10 Hz), -111.74 (2F, t, *J* = 14 Hz), -121.68 (2F, m), -122.22 (2F, m), -122.39 (2F, m), -123.24 (2F, m), and -126.63 (2F, m); IR (KBr) 1692vs, 1300-1100vs, 946s, and 654s cm^{-1}; MS (EI) *m/z* (rel intensity) 524 (M^+, 3), 523 (M^+-1, 6), 171 (100), 155 (49), and 127 (8). HRMS Found: *m/z* 524.0069. Calcd for $C_{15}H_5F_{17}O$: M, 524.0068.

Reaction of 1a with Dimethyloxosulfonium Methylide

To a solution of dimethyloxosulfonium methylide[15] (10 mmol) in DMSO (15 ml) was added a solution of quinol **1a** (2.640 g, 5 mmol) in DMSO at 5-10 °C. The mixture was stirred for 2 h at room temperature and then aq NH_4Cl was added. The mixture was extracted with ether (3 x 30 ml). The ethereal phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2/ether) to give 0.554 g of **4a**, 0.390 g of a crude mixture of 5-hydroxy-3-(perfluoroheptyl)benzo[b]furan (**16**) and 5-hydroxy-4-[(E)-perfluoro-1-octenyl]-2,3-dihydrobenzo[b]furan (**17**), and 0.528 g of **1a**. Purification of **16** and **17** was performed by preparative GPC to afford 0.125 g of **16** and 0.077 g of **17**. **16**: colorless needles, mp 77-78 °C (CH_2Cl_2/hexane); ^1H NMR δ = 5.32 (1H, br s), 6.94 (1H, dd, *J* = 8.8 and 2.4 Hz), 7.08 (1H, m), 7.41 (1H, d, *J* = 8.8 Hz), and 7.89 (1H, s); ^{13}C NMR δ = 105.64, 105-125 (7C), 111.80 (t, *J* = 28 Hz), 112.67, 114.81, 124.40 (t, *J* = 3 Hz), 147.10 (t, *J* = 9 Hz), 150.50, and 152.52; ^{19}F NMR δ = -81.31 (3F, t, *J* = 10 Hz), -108.25 (2F, t, *J* = 14 Hz), -121.93 (2F, m), -122.57 (4F, m), -123.21 (2F, m), and -126.61 (2F, m); IR (KBr) 3220vs, 1600s, 1580s, 1456s, 1370s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 503 (M^++1, 7), 502 (M^+, 37), and 183 (100). Anal Calcd for $C_{15}H_5F_{15}O_2$: C, 35.88; H, 1.00%. Found: C, 35.76; H, 1.04%. **17**: pale yellow crystals, mp 71-73 °C (CH_2Cl_2/hexane); ^1H NMR (acetone-d_6) δ = 3.17 (2H, t, *J* = 8.6 Hz), 4.54 (2H, d, *J* = 8.6 Hz), 6.76 (2H, m), and 8.77 (1H, br s); ($CDCl_3$) δ = 3.12 (2H, t, *J* = 8.6 Hz), 4.53 (2H, d, *J* = 8.6 Hz), 5.25 (1H, br s), 6.60 (1H, d, *J* = 8.8 Hz), and 6.73 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (acetone-d_6) δ = 30.44 (d, *J* = 1 Hz), 72.51, 105-125 (6C), 112.0 (m), 114.64 (d, *J* = 2 Hz), 116.51, 129.59, 138.05 (ddt, *J* = 243, 49, and 28 Hz), 151.24, 154.10 (dd, *J* = 261 and 46 Hz), and 154.75 (d, *J* = 1 Hz); ^{19}F NMR δ = -80.64 (3F, tt, *J* = 10 and 2 Hz), -116.21 (2F, m), -121.64 (2F, m), -122.37 (2F, m), -123.25 (2F, m), -125.75 (2F, m), -129.47 (1F, ttt, *J* = 140, 27, and 6 Hz), and -163.07 (1F, dm, *J* = 140 Hz); MS (EI) *m/z* (rel intensity) 517 (M^++1, 15), 516 (M^+, 100), 497 (22), 477 (3), 227 (49), 197 (20), and 183 (22). Anal Calcd for $C_{16}H_7F_{15}O_2$: C, 37.23; H, 1.37%. Found: C, 36.79; H, 1.32%.

Acyloin Rearrangement; General Procedure

To a solution of quinol **1** (1 mmol) in 2 ml of DMSO was added 11 mg of *t*-BuOK at room temperature under a nitrogen atmosphere. The mixture was heated at 80 °C with stirring. After the mixture was heated for the indicated period (Table 2), ether (20 ml) and water (10 ml) were added. The organic phase was separated and the aqueous phase was extracted with ether (3 x 20 ml). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2/ether). Some of hydroquinones were protected as diacetates: The obtained hydroquinone **4** was dissolved in 1 ml of pyridine. To the mixture was added 1 ml of acetic anhydride at room temperature. After the mixture was stirred overnight, ether (20ml) and water (10 ml) were added. The organic phase was separated and the

aqueous phase was extracted with ether (3 x 20 ml). The ethereal extract was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2/ether) to give a diacetate in a near quantitative yield.

2-(Perfluorooctyl)hydroquinone (4a). Colorless crystals, mp 119-120 °C (ether/hexane); ^1H NMR (acetone-d_6) δ = 6.91 (3H, m), 8.19 (1H, s), and 8.57 (1H, s); ^{13}C NMR (acetone-d_6) δ = 105-125 (8C), 115.85 (t, *J* = 9 Hz), 115.85 (t, *J* = 23 Hz), 119.96, 122.26, 150.97 (t, *J* = 3 Hz), and 151.51; IR (KBr) 3368vs, 1460s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 528 (M^+, 40), 508 (9), 201 (9), 189 (29), 159 (100), and 137 (17). Anal Calcd for $C_{14}H_5F_{17}O_2$: C, 31.84; H, 0.95%. Found: C, 31.48; H, 0.81%.

1,4-Diacetoxy-2-(perfluorooctyl)benzene. Colorless crystals, mp 94-95 °C; ^1H NMR δ = 2.29 (3H, s), 2.32 (3H, s), 7.24 (1H, d, *J* = 9.8 Hz), 7.35 (1H, s), and 7.36 (1H, d, *J* = 9.8 Hz); ^{13}C NMR δ = 20.44, 20.83, 105-125 (8C), 121.80 (t, *J* = 24 Hz), 122.19 (t, *J* = 8 Hz), 125.85, 126.54, 146.10 (t, *J* = 3 Hz), 147.95, 168.71, and 168.73; ^{19}F NMR δ = -81.26 (3F, tt, *J* = 10 and 2 Hz), -109.40 (2F, t, *J* = 13 Hz), -121.62 (2F, m), -122.0--122.4 (6F, m), -123.20 (2F, m), and -126.59 (2F, m); IR (KBr) 1762vs, 1500s, 1428s, 1372s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 612 (M^+, 1), 570 (10), 528 (100), 189 (9), and 159 (70). Anal Calcd for $C_{18}H_9F_{17}O_4$: C, 35.31; H, 1.48%. Found: C, 35.02; H, 1.35%.

2-(Perfluorohexyl)hydroquinone (4b). Colorless crystals, mp 112-113 °C (ether/hexane); ^1H NMR (acetone-d_6) δ = 6.90 (3H, m), 8.22 (1H, s), and 8.62 (1H, s); ^{13}C NMR (acetone-d_6) δ = 105-125 (6C), 115.67 (t, *J* = 9 Hz), 115.67 (t, *J* = 23 Hz), 119.78, 122.10, 150.72 (t, *J* = 3 Hz), and 151.32; ^{19}F NMR (acetone-d_6) δ = -81.70 (3F, tt, *J* = 10 and 2 Hz), -107.41 (2F, m), -120.75 (2F, m), -121.44 (2F, m), -122.35 (2F, m), and -125.84 (2F, m); IR (KBr) 3368vs, 1458s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 429 (M^++1, 4), 428 (M^+, 31), 390 (3), 201 (4), 189 (11), and 159 (100). Anal Calcd for $C_{12}H_5F_{13}O_2$: C, 33.66; H, 1.18%. Found: C, 33.55; H, 1.33%.

2-(Perfluoroisopropyl)hydroquinone (4c). Colorless viscous oil; ^1H NMR δ = 6.16 (1H, br d, *J* = 8.5 Hz), 6.40 (1H, br s), 6.79 (1H, d, *J* = 8.9 Hz), 6.86 (1H, dd, *J* = 8.9 and 2.8 Hz), and 6.96 (1H, d, *J* = 2.8 Hz); ^{13}C NMR δ = 93.31 (d-septet, *J* = 232 and 34 Hz), 112.96 (dm, *J* = 17 Hz), 114.08 (d, *J* = 13 Hz), 119.79, 120.03, 120.61 (qd, *J* = 288 and 28 Hz), 148.33 (d, *J* = 2 Hz), and 148.99 (d, *J* = 3 Hz); ^{19}F NMR δ = -75.11 (6F, d, *J* = 5 Hz) and -178.17 (F, m); IR (neat) 3340vs, 1516s, 1454s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 279 (M^++1, 9), 278 (M^+, 100), 276 (13), 258 (6), 248 (14), 238 (18), 230 (24), 220 (62), 189 (40), 161 (39), and 82 (71).

2-Methyl-5-(perfluorooctyl)hydroquinone (4d). Colorless crystals, mp 95-97 °C (ether/hexane); ^1H NMR δ = 2.23 (3H, s), 4.68 (1H, br s), 5.29 (1H, br s), 6.71 (1H, m), and 6.85 (1H, m); ^{13}C NMR δ = 16.06, 105-125 (8C), 112.17 (t, *J* = 9 Hz), 114.01 (t, *J* = 22 Hz), 122.68, 129.13, 147.04 (t, *J* = 3 Hz), and 148.65; ^{19}F NMR δ = -81.39 (3F, tt, *J* = 10 and 2 Hz), -108.35 (2F, t, *J* = 14 Hz), -121.7--122.3 (8F, m), -123.04 (2F, m), and -126.45 (2F, m); IR (KBr) 3368vs and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 542 (M^+, 100), 522 (11), 502 (8), 203 (15), 173 (29), and 125 (7). HRMS Found: *m/z* 542.0164. Calcd for $C_{15}H_7F_{17}O_2$: M, 542.0175.

2-Methyl-6-(perfluorooctyl)hydroquinone (4e). Colorless crystals, mp 123-125 °C (ether/hexane); ^1H NMR δ = 2.24 (3H, s), 4.46 (1H, br s), 5.12 (1H, br s), 6.77 (1H, s), and 6.78 (1H, s); ^{19}F NMR δ = -81.34 (3F, tt, *J* = 10 and 3 Hz), -108.32 (2F, t, *J* = 14 Hz), -121.77 (2F, m), -122.12 (6F, m), -123.03 (2F, m), and -126.43 (2F, m); IR (KBr) 3340vs, 1420s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 543

(M^++1, 10), 542 (M^+, 49), 504 (7), 486 (7), 484 (8), 442 (8), 215 (11), 203 (26), and 173 (100). HRMS Found: *m/z* 542.0148. Calcd for $C_{15}H_7F_{17}O_2$: M, 542.0175.

2,5-Diacetoxy-1-methyl-3-(perfluorooctyl)benzene. Colorless crystals, mp 110-111 °C; ^{1}H NMR δ = 2.23 (3H, s), 2.28 (3H, s), 2.33 (3H, s), 7.11 (1H, s), and 7.26 (1H, s); ^{13}C NMR δ = 16.43, 20.62, 20.66, 105-125 (8C), 119.19 (t, *J* = 24 Hz), 122.58 (t, *J* = 8 Hz), 127.18, 136.61, 145.96 (t, *J* = 3 Hz), 146.71, 168.57, and 168.85; ^{19}F NMR δ = -81.24 (3F, tt, *J* = 9 and 2 Hz), -109.21 (2F, m), -121.75 (2F, m), -122.22 (6F, m), -123.23 (2F, m), and -126.61 (2F, m); IR (KBr) 1768vs, 1372s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 626 (M^+, 0.6), 607 (0.7), 542 (100), and 173 (30). HRMS Found: *m/z* 626.0400. Calcd for $C_{19}H_{11}F_{17}O_4$: M, 626.0386.

3,5-Dimethyl-2-(perfluorooctyl)hydroquinone (4f). Colorless crystals, mp 121-123 °C (ether/hexane); ^{1}H NMR δ = 2.25 (3H, s), 2.30 (3H, t, *J* = 3.4 Hz), 4.42 (1H, br s), 5.38 (1H, t, *J* = 8.6 Hz), and 6.66 (1H, s); ^{13}C NMR δ = 13.15 (t, *J* = 3 Hz), 16.43, 105-125 (8C), 118.27, 124.26 (t, *J* = 24 Hz), 124.55 (t, *J* = 3 Hz), 129.75, 146.63, and 149.20 (t, *J* = 4 Hz); ^{19}F NMR δ = -81.22 (3F, t, *J* = 10 Hz), -101.45 (2F, m), -120.40 (2F, m), -122.2 (6F, m), -123.18 (2F, m), and -126.59 (2F, m); IR (KBr) 3300vs, 1454s, 1412s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 556 (M^+, 49), 508 (10), 217 (6), 197 (21), 187 (100), 139 (21), and 111 (7). HRMS Found: *m/z* 556.0296. Calcd for $C_{16}H_9F_{17}O_2$: M, 556.0330.

2-t-Butyl-5-(perfluorooctyl)hydroquinone (4i). Colorless crystals, mp 86-87 °C (ether/hexane); ^{1}H NMR δ = 1.39 (9H, s), 4.88 (1H, br s), 5.27 (1H, br s), 6.69 (1H, s), and 6.90 (1H, s); ^{19}F NMR δ = -80.57 (3F, tt, *J* = 10 and 2 Hz), -107.13 (2F, m), -120.63 (2F, m), -121.0--121.5 (6F, m), -122.20 (2F, m), and-125.67 (2F, m); IR (KBr) 3612s, 3448s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 585 (M^++1, 16), 584 (M^+, 80), 569 (59), 553 (100), 541 (28), 525 (37), and 199 (17). HRMS Found: *m/z* 584.0643. Calcd for $C_{18}H_{13}F_{17}O_2$: M, 584.0644.

5-Methyl-5-perfluorooctyl-2-cyclohexene-1,4-dione (25e'). ^{1}H NMR δ = 1.47 (3H, s), 2.69 (1H, dd, *J* = 17.1 and 1.8 Hz), 3.23 (1H, d, *J* = 17.1 Hz), and 6.75 (2H, s); ^{19}F NMR δ = -81.23 (3F, tt, *J* = 10 and 2 Hz), -110.04 (1F, dm, *J* = 284 Hz), -114.10 (1F, dm, *J* = 284 Hz), -117.42 (2F, m), -121.8--122.4 (6F, m), -123.22 (2F, m), and -126.60 (2F, m).

2,6-Dimethyl-6-perfluorooctyl-2-cyclohexene-1,4-dione (25g). Colorless crystals, mp 72-73 °C (ether/hexane); ^{1}H NMR δ = 1.55 (3H, s), 2.06 (3H, d *J* = 1.5 Hz), 2.73 (1H, dd, *J* = 17.2 and 2.1 Hz), 3.27 (1H, d, *J* = 17.2 Hz), and 6.68 (1H, q, *J* = 1.5 Hz); ^{13}C NMR δ = 16.93, 19.35, 45.10, 54.18 (t, *J* = 20 Hz), 105-125 (8C), 138.05, 150.20, 193.00, and 194.03; ^{19}F NMR δ = -81.25 (3F, t, *J* = 10 Hz), -109.96 (1F, dm, *J* = 284 Hz), -114.44 (1F, dm, *J* = 284 Hz), -117.73 (2F, m), -121.8--122.6 (6F, m), -123.22 (2F, m), and -126.61 (2F, m); IR (KBr) 1702vs, 1684vs, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 556 (M^+, 3), 537 (2), 137 (100), 96 (58), and 68 (41). Anal Calcd for $C_{16}H_9F_{17}O_2$: C, 34.55; H, 1.63%. Found: C, 34.50; H, 1.84%.

2,5-Dimethyl-5-perfluorooctyl-2-cyclohexene-1,4-dione (25h). Colorless crystals, mp 77-78 °C (ether/hexane); ^{1}H NMR δ = 1.52 (3H, s), 2.05 (3H, d *J* = 1.5 Hz), 2.75 (1H, d, *J* = 17.0 Hz), 3.29 (1H, d, *J* = 17.0 Hz), and 6.69 (1H, q, *J* = 1.5 Hz); ^{13}C NMR δ = 15.94, 19.20 (m), 44.85, 54.63 (t, *J* = 20 Hz), 105-125 (8C), 137.04, 151.15, 192.75, and 193.89; ^{19}F NMR δ = -81.31 (3F, tt, *J* = 10 and 2 Hz), -110.0 (1F, dm, *J* = 285 Hz), -114.0 (1F, dm, *J* = 285Hz), -117.46 (2F, m), -122.0--122.5 (6F, m), -123.22 (2F, m), and -126.63 (2F, m); IR (KBr) 1692vs, 1680vs, 1626m, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel

intensity) 556 (M^+, 5), 537 (3), 137 (100), 96 (68), and 68 (50). Anal Calcd for $C_{16}H_9F_{17}O_2$: C, 34.55; H, 1.63%. Found: C, 34.34; H, 1.68%.

2,3,5,6-Tetramethyl-5-perfluorooctyl-2-cyclohexene-1,4-dione (25m). Colorless crystals, mp 67-68 °C (*cis:trans* = 5:4); ^1H NMR (*cis* isomer) δ = 1.42 (3H, dd, *J* = 6.7 and 3.3 Hz), 1.61 (3H, s), 2.04 (3H, s), 2.06 (3H, s), and 2.73 (1H, q, *J* = 6.7 Hz); (*trans* isomer) δ = 1.15 (3H, dd, J = 7.3 Hz), 1.43 (3H, br s), 2.02 (6H, s), and 3.23 (1H, q, *J* = 7.3 Hz); ^{19}F NMR δ = -81.34 (both 3F, t, *J* = 10 Hz), -106.1 (1F of *cis* isomer, dm, *J* = 285 Hz), -107.1 (1F of *trans* isomer, dm, *J* = 282 Hz), -112.6 (1F of *trans* isomer, m), -118.8 (1F of *cis* isomer, m), -119--125 (both 10F, m), and -126.68 (both 2F, m); IR (KBr) 1686vs, 1638vs, 1452s, 1376s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 584 (M^+, 4), 568 (7), 564 (17), 195 (34), 167 (48), 165 (100), and 136 (36). Anal Calcd for $C_{18}H_{13}F_{17}O_2$: C, 37.00; H, 2.24%. Found: C, 36.92; H, 2.37%.

(R,S*)-7-Hydroxy-2,3,4a,5,6,8,9a-heptamethyl-1,4,4a,9a-tetrahydroxanthene-1,4-dione.* Colorless crystals, mp 210-210.5 °C (CH_2Cl_2/hexane; lit. 208-209 °C[11a] and 207.5-208 °C[11b]). ^1H NMR δ = 1.27 (3H, s), 1.44 (3H, s), 2.01 (9H, s), 2.14 (3H, s), 2.16 (3H, s), 2.43 (1H, d, *J* = 16.8 Hz), 2.97 (1H, d, *J* = 16.8 Hz), and 4.28 (1H, s).

1,4-Bis(perfluorooctyl)-2,5-cyclohexadiene-1,4-diol (24). Colorless crystals, mp 155-156 °C (ether/hexane); ^1H NMR (acetone-d_6) δ = 5.98 (2H, s) and 6.33 (4H, s); ^{13}C NMR (acetone-d_6) δ = 74.93 (t, *J* = 20 Hz), 105-125 (16C), and 134.31; ^{19}F NMR (acetone-d_6) δ = -80.57 (6F, t, *J* = 10 Hz), -118.27 (4F, m), -118.95 (4F, m), -121.1--121.4 (12F, m), -122.20 (4F, m), and -125.65 (4F, m); IR (KBr) 3604s, 3420vs, 1372s, 1332s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 948 (M^+, 0.4), 947 (M^+, 0.8), 930 (2), 929 (1), 928 (4), 910 (12), 908 (5), 529 (100), and 110 (34). Anal Calcd for $C_{22}H_6F_{34}O_2$: C, 27.87; H, 0.64%. Found: C, 27.54; H, 0.64%.

3-Methyl-3-perfluorooctyl-1-propylpyrrolidine-2,5-dione (26). Colorless crystals, mp 48-49 °C (CH_2Cl_2/hexane); ^1H NMR δ = 0.91 (3H, t, *J* = 7.3 Hz), 1.60 (2H, m), 1.63 (3H, s), 2.57 (1H, d, *J* = 18.0 Hz), 3.17 (1H, d, *J* = 18.0 Hz), and 3.52 (1H, t, *J* = 7.3 Hz); ^{13}C NMR δ = 11.01, 19.53, 20.67, 37.84 (t, *J* = 3 Hz), 49.01 (t, *J* = 22 Hz), 105-125 (8C), 173.00, and 173.69 (t, *J* = 3 Hz); ^{19}F NMR δ = -81.24 (3F, tt, *J* = 10 and 2 Hz), -114.53 (2F, m), -117.96 (2F, m), -122.21 (6F, m), -123.21 (2F, m), and -126.60 (2F, m); IR (KBr) 1782s, 1710vs, 1408s, 1388s, 1370s, 1348s, 1328s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 573 (M^+, 15), 532 (62), 487 (6), 441 (5), 153 (15), 124 (32), and 91 (100). Anal Calcd for $C_{16}H_{12}F_{17}NO_2$: C, 33.52; H, 2.11; N, 2.44%. Found: C, 33.53; H, 1.96; N, 2.52%.

Oxidation of Hydroquinone 4 to Quinone 15

To a solution of hydroquinone **4** in acetonitrile (5 ml) was added an aqueous solution of CAN (1.159 g, 2.1 mmol) at 0 °C. After 10 min, water (10 ml) and ether (20 ml) were added. The organic phase was separated and the aqueous phase was extracted with ether (3 x 20 ml). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2/ether).

2-Perfluorooctyl-1,4-benzoquinone (15a). Yellow crystals, mp 77-78 °C (ether/hexane); ^1H NMR δ = 6.88 (1H, d, *J* = 10.0 Hz), 6.92 (1H, dd, *J* = 10.0 and 2.0 Hz), and 7.14 (1H, m); ^{13}C NMR δ = 105-125 (8C), 135.04 (t, *J* = 22 Hz), 136.03, 137.60, 138.20 (t, *J* = 8 Hz), 181.10 (t, *J* = 1 Hz), and 185.13; ^{19}F NMR δ = -81.30 (3F, tt, *J* = 10 and 2 Hz), -112.23 (2F, m), -120.78 (2F, m), -122.05 (2F, m), -122.32 (4F, m), -123.20 (2F, m), and -126.63 (2F, m); IR (KBr) 1670vs and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel

intensity) 526 (M^+, 6), 507 (5), 488 (3), 169 (7), 157 (69), and 129 (100). Anal Calcd for $C_{14}H_3F_{17}O_2$: C, 31.96; H, 0.57%. Found: C, 31.87 H, 0.49%.

2-Methyl-5-perfluorooctyl-1,4-benzoquinone (15d). Yellow crystals, mp 48-49 °C (ether/hexane); ^1H NMR δ = 2.13 (3H, d, *J* = 1.5 Hz), 6.76 (1H, m), and 7.07 (1H, m); ^{13}C NMR δ = 16.14, 105-125 (8C), 133.07, 135.11 (t, *J* = 22 Hz), 138.30 (t, *J* = 8 Hz), 147.28, 181.88, and 185.03; ^{19}F NMR δ = -81.26 (3F, tt, *J* = 10 and 2 Hz), -111.74 (2F, t, *J* = 14 Hz), -120.63 (2F, m), -121.5--122.5 (6F, m), -123.18 (2F, m), and -126.59 (2F, m); IR (KBr) 1662vs, 1618s, 1372s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 540 (M^+, 37), 512 (13), 203 (8), 173 (49), 143 (100), and 115 (22). HRMS Found: *m/z* 540.0077. Calcd for $C_{15}H_5F_{17}O_2$: M, 540.0018.

3,5-Dimethyl-2-perfluorooctyl-1,4-benzoquinone (15f). Yellow crystals, mp 59-60 °C (ether/hexane); ^1H NMR δ = 2.03 (3H, d, *J* = 1.5 Hz), 2.23 (3H, t, *J* = 3.7 Hz), and 6.57 (1H, q, *J* = 1.5 Hz); ^{19}F NMR δ = -81.23 (3F, t, *J* = 10 Hz), -105.12 (2F, m), -120.39 (2F, m), -122.1--122.4 (6F, m), -123.18 (2F, m), and -126.58 (2F, m); IR (KBr) 1666vs, 1612s, and 1300-1100vs cm^{-1}; MS (EI) *m/z* (rel intensity) 554 (M^+, 7), 526 (6), 185 (25), 157 (100), and 129 (19). HRMS Found: *m/z* 554.0219. Calcd for $C_{16}H_7F_{17}O_2$: M, 554.0253.

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