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1,2-Migration of Perfluoroalkyl Groups in Anionotropic Rearrangement. The Acyloin Rearrangement of 4-Perfluoroalkyl-4-quinols

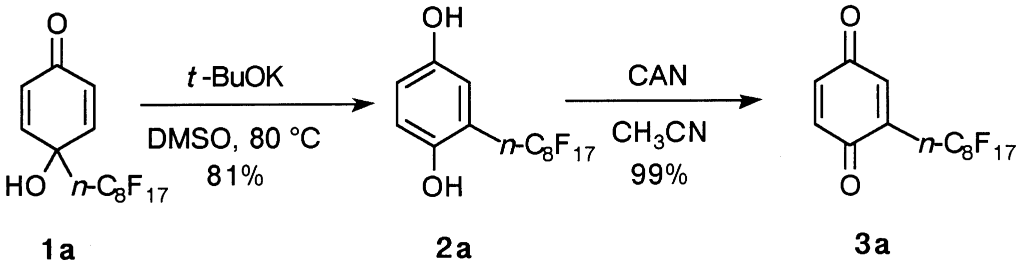
Hidemitsu UNO,* Ayumi YAYAMA, and Hitomi SUZUKI*,†
Advanced Instrumentation Center for Chemical Analysis, Ehime University, Bunkyo-cho, Matsuyama 790
†Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

Treatment of 4-perfluoroalkyl-4-quinols with a catalytic amount of potassium *t*-butoxide gave 2-(perfluoroalkyl)hydroquinones or 5-perfluoroalkyl-2-cyclohexene-1,4-diones in good to moderate yields depending upon the substitution pattern of the quinols. Similarly, 2-hydroxy-3-methyl-2-perfluorooctyl-1-propyl-3-pyrrolin-5-one underwent the base-induced rearrangement to afford a perfluoroalkylated succinimide derivative.

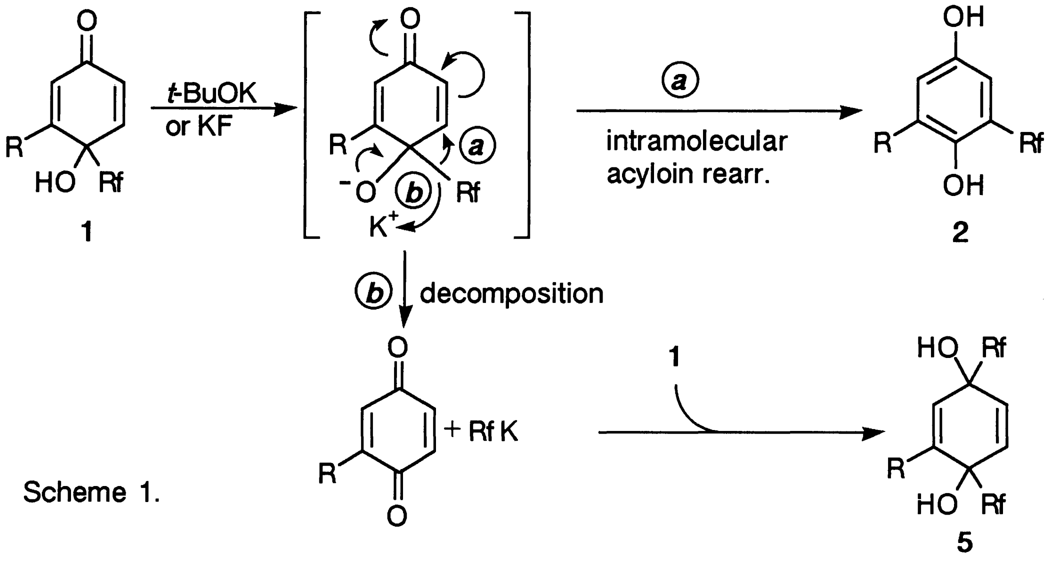
Although the acid- or base-induced migration of an alkyl group from one carbon atom to another has been recorded as vast numbers of anionotropic and cationotropic rearrangements, there is known no counterpart of perfluoroalkyl group so far.1) Accumulation of electronegative fluorine atoms on a carbon atom suppresses its migration toward an electrophilic center, while the ease of fluorine atom to leave as fluoride anion hampers the migration toward a nucleophilic terminus.2) However, we wish now to report the first example of the base-induced 1,2-shift of perfluoroalkyl groups in anionotropic rearrangement, i.e. the acyloin rearrangement of 4-perfluoroalkyl-4-quinols.3)

Treatment of 4-perfluorooctyl-4-hydroxy-2,5-cyclohexadien-1-one (**1a**, 4-perfluorooctyl-4-quinol)4) with 10 mol% of potassium *t*-butoxide in DMSO at 80 °C led to gradual disappearance of **1a** (within 3 h) to afford a new product of the same composition in 81% yield. This compound was easily identified as 2-(perfluorooctyl)hydroquinone (**2a**) on the basis of its IR and NMR spectra, elemental analysis, and conversion to 2-perfluorooctyl-1,4-benzoquinone (**3a**) (Eq. 1).

At room temperature, the rearrangement was quit slow even in the presence of an equivalent amount of base. Sodium methylsulfinylmethanide and spray-dried KF were also effective as the base. Polar aprotic solvents such as DMF, HMPA, and sulfolane were successfully employed, but in THF, dioxane, and *t*-BuOH the rearrangement did not take place and a significant part of **1a** was recovered intact (57-76%). A variety of 4-perfluoroalkyl-4-quinols were subject to the acyloin rearrangement (Eq. 2) and the results are listed in Table 1.



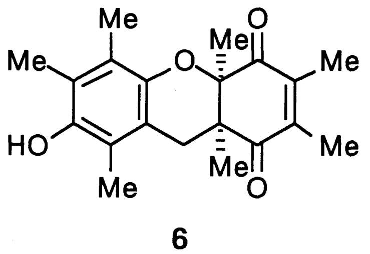
(1)



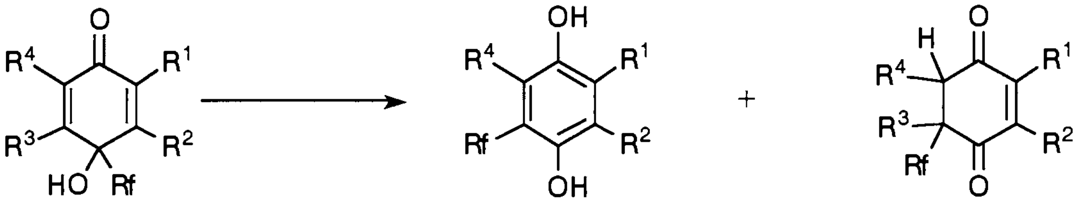
Scheme 1.

As shown in the table, the perfluoroalkyl group resisted to move to the adjacent position occupied by methyl group (entries 8 and 12).[5] When both adjacent positions were occupied (entry 11), the rearrangement led to the formation of cyclohexenedione **4f**. Low yields observed in the reaction of alkyl-substituted quinols **1c**-**1h** may be attributed to the concurrent decomposition of the quinol anion into the parent quinone and perfluoroalkyl anion (Scheme 1). In support of this, the presence of a small amount of 1,4-bis(perfluorooctyl)-2,5-cyclohexadiene-1,4-diol (**5a**; R=H) was confirmed by GC-MS analysis of the crude product mixture from **1a**. In addition, when the quinol **1a** was heated with base in the presence of 2,5-dimethyl-1,4-benzoquinone (5 equiv), 2,5-dimethyl-5-perfluorooctyl-2-cyclohexene-1,4-dione (**4g**) was obtained besides the expected **2a**. However, the acyloin rearrangement itself is an intramolecular process, since no crossover was observed when a mixture of **1b** and **1c** was treated with base under the usual conditions. The rearrangement of quinols **1c** and **1d** gave perfluoroalkylated hydroquinones **2c** and **2d** respectively in comparable yields, which may rule out the decomposition of the quinol anion into a quinone anion radical and a perfluoroalkyl radical as possible intermediates. Recombination of these two intermediates should lead to a mixture of **2c** and **2d**.

Highly substituted quinol **1k** underwent the rearrangement to give a diastereomeric mixture of cyclohexenedione **4k** (*trans*:*cis*=4:5) in 40% yield along with duroquinone (31%) and its dimerization product **6** (21%).[6] Stereochemical determination of **4k** was made on $^5J_{\mathrm{HF}}$ coupling constants between the methyl (R^4) and perfluorooctyl groups. Proton NMR spectrum of the major isomer showed the methyl signals at δ=1.43 as double of doublets (J=6.7 and 3.4 Hz) due to the "through-space" long-range coupling with perfluorooctyl group,[7] while the methyl signals of the minor isomer appeared at δ=1.16 as sharp doublets (J=7.3 Hz). The compounds **4k** were rather unstable and gradually decomposed to duroquinone, when stood in duteriochloroform at room temperature. Interestingly, quinols **1i** and **1j** derived from 2-methoxy-1,4-benzoquinone and 1,4-naphthoquinone respectively did not undergo rearrangement even after prolonged reaction time.



6



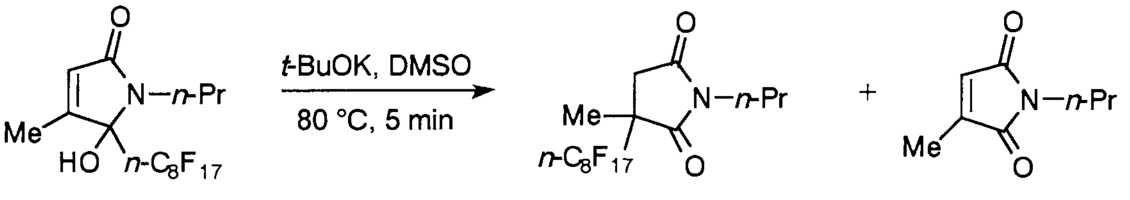
1 Rf = n-C_nF_{2n+1} 2 4

(2)

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

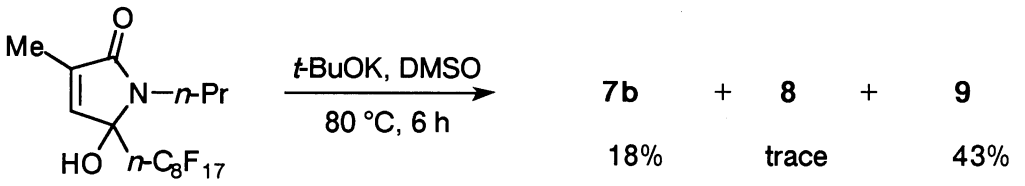
Entry	Quinol						Conditions			Yield/%[a]		
	1	R^1	R^2	R^3	R^4	Rf(n)	*t*-BuOK (mol%)	Temp °C	Time h	1	2	4
1	**a**	H	H	H	H	8	10	80	3	-	81	-
2	**a**	H	H	H	H	8	10	r.t.	144	30	39	-
3	**a**	H	H	H	H	8	100	r.t.	168	trace	60	-
4	**a**	H	H	H	H	8	10[b]	80	11	4	69	-
5	**a**	H	H	H	H	8	500[c]	80	3	-	20[d]	-
6	**a**	H	H	H	H	8	10[c]	80	3	trace	79[d]	-
7	**b**	H	H	H	H	6	10	80	3	-	64	-
8	**c**	Me	H	H	H	8	10	80	3	-	47	-
9	**d**	H	Me	H	H	8	10	80	0.5	-	46	-
10	**e**	Me	H	H	Me	8	10	80	24	40	4	-
11	**f**	H	Me	Me	H	8	10	80	0.5	-	-	66
12	**g**	Me	H	Me	H	8	10	80	0.5	-	-	35
13	**h**	*t*-Bu	H	H	H	8	10	80	24	62	23	-
14	**i**	H	OMe	H	H	4	10	80	24	58	-	-
15	**j**	-CH=CH-CH=CH-		H	H	6	10	80	6	64	-	-
16	**k**	Me	Me	Me	Me	8	10	80	1	-	-	40[e]

a) Isolated yield. b) Sodium methylsulfinylmethanide was used as a base. c) Potassium fluoride was used as a base. d) 1,4-Bis(perfluorooctyl)-2,5-cyclohexadiene-1,4-diol (**5a**) was obtained in 5% yield. e) Diastereomer mixture (*trans*:*cis*=4:5). Duroquinone and its dimer **6** were also obtained in 31% and 21% yields, respectively.



7a **8**; 41% **9**; 20%

(3)



7b

(4)

As an extension of this perfluoroalkyl migration, the reaction of cyclic enamides was investigated. A brief heating (5 min) of **7a** at 80 °C in DMSO in the presence of potassium *t*-butoxide (10 mol%) gave the perfluoroalkyl migration product **8** and citraconimide **9** (Eq. 3). On a similar treatment, the isomeric enamide **7b** did not rearrange but simply decomposed to the imide **9** (Eq. 4).

In summary, the base-induced acyloin rearrangement of 4-perfluoroalkyl-4-quinols gave 2-(perfluoroalkyl)hydroquinones in acceptable yields. This finding provides not only the first example of perfluoroalkyl 1,2-shift but also the first formal 1,4-addition of perfluoroalkyl anionic species to quinones.[8)]

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