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Perfluoroalkyl-thwarted Rearrangement of Quinol Esters. Formation of Catechol Derivatives via 1,3-Migration of Acyloxyl Group

Hitomi SUZUKI,* Yasukazu SHIRAISHI, Kazuhiro SHIMOKAWA,† and Hidemitsu UNO*

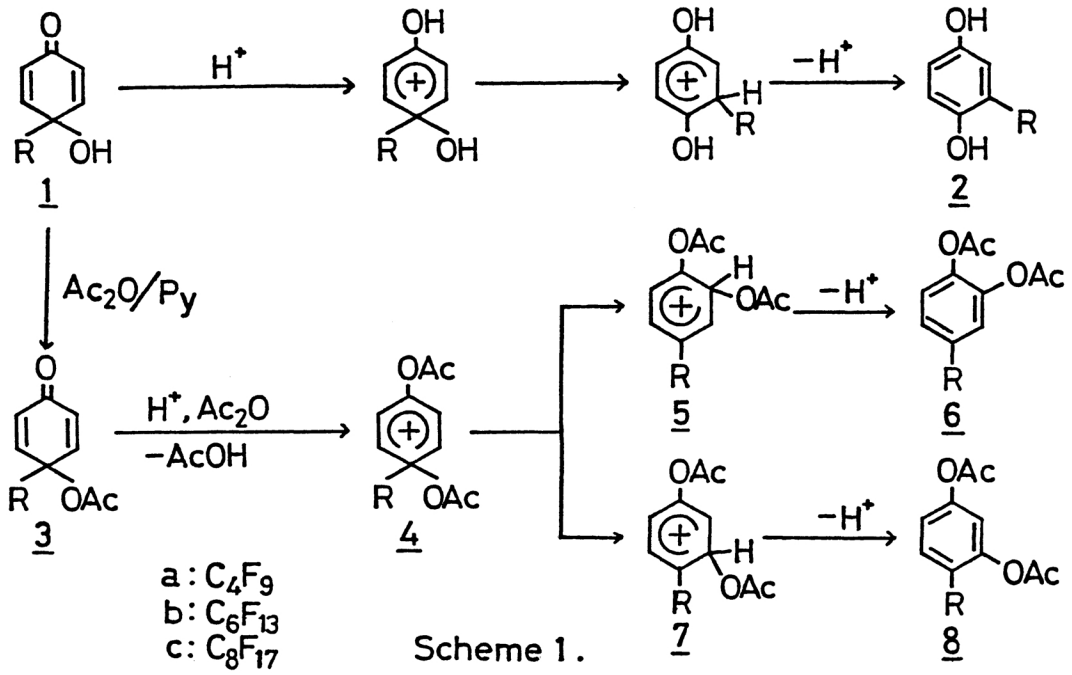
Department of Chemistry, Faculty of Science,
Advanced Instrumentation Center for Chemical Analysis,
Ehime University, Bunkyo-cho, Matsuyama 790

†Research and Development Department, Chemical Division,
Daikin Industries, Ltd., Nishi Hitotsuya, Settsu 566

Treatment of 4-perfluoroalkyl-4-quinols with acetic anhydride-sulfuric acid was found to lead to 1,2- and 1,3-migration of acetoxyl group in initially formed quinol acetates followed by aromatization to give a mixture of 4-perfluoroalkylresorcinol diacetate and 4-perfluoroalkylcatechol diacetate.

On treatment with sulfuric acid in aqueous methanol, 4-alkyl-4-hydroxy-2,5-cyclohexadienones (**1**; 4-alkyl-4-quinols) undergo rearrangement followed by aromatization to yield alkylhydroquinones **2**. The reaction has been known as the quinol rearrangement.[1] In acetic anhydride-sulfuric acid, the reaction takes another course to afford 4-alkylresorcinol diacetate **8** via the 1,2-migration of an ester group in initially formed acetate **3**.[2] Acyloxyl group usually migrates in preference to alkyl group.[3] Perfluoroalkyl group attached to the cation center is known to destabilize a carbenium ion enormously,[4,5] and forestall the Wagner-Meerwein type rearrangement which proceeds via a cation intermediate.[6] Therefore, it is natural concequence to expect that 4-perfluoroalkyl-4-quinonls **1a**-**c** will rearrange in acetic anhydride-sulfuric acid to give 4-perfluoroalkylresorcinol diacetate **8** as a single product. This was found not necessarily to be the case, however. We wish to report herein the first example of the acid-catalyzed conversion of quinols into catechol derivatives via the 1,3-acetoxyl migration.

When quinol **1a** or its ester **3a** was stirred in acetic anhydride containing sulfuric acid at room temperature overnight, two products were obtained as an intimate 1:1 mixture in 98-100% yields. Both compounds had the same composition $C_{14}H_9O_4F_9$, thus to be isomeric each other. One compound was identified as the expected 4-perfluorobutylresorcinol diacetate (**8a**) on the basis of ^1H, ^{13}C, and ^{19}F NMR spectra as well as by its conversion to 4-perfluorobutanoylresorcinol (**13**). The structure of diacetate **8a** was unambiguously established by COSY (^1H-^{13}C) and 2D-INADEQUATE (^{13}C-^{13}C) NMR techniques. To our surprise, however, another product was proved to possess the catechol skeleton **6** by NMR spectral analysis and transformation into o-quinone **11** as shown in Scheme 2.

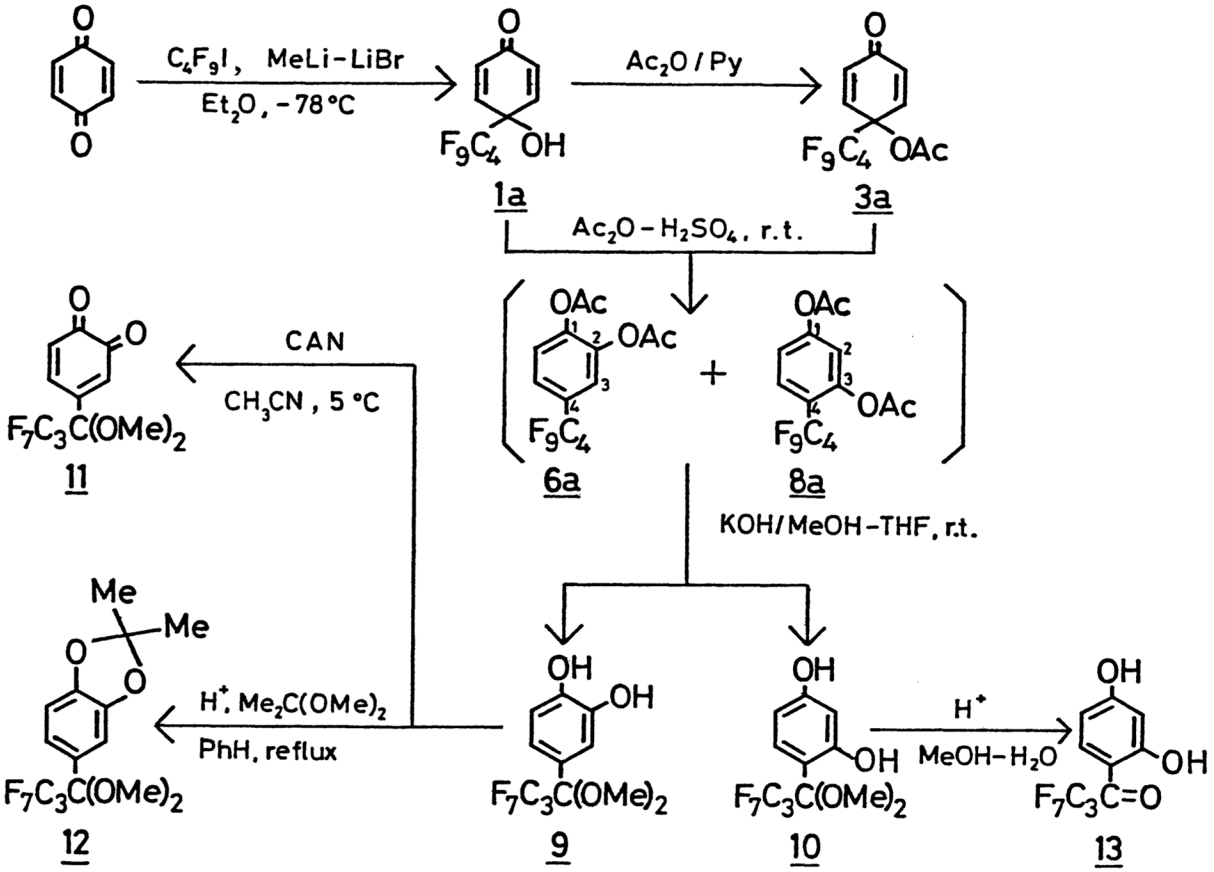


Scheme 1.

Thus, when the mixture of rearranged products **6a** and **8a** was stirred with KOH in THF-methanol at room temperature, cleavage of ester groups occurred with simultaneous methanolysis of perfluorobutyl group to produce acetals **9** and **10** which could be separated by chromatography on silica gel. On refluxing in aqueous methanol containing p-toluenesulfonic acid, the latter compound was deacetalized to give ketone **13**. Treatment of the former compound with ammonium cerium(IV) nitrate in acetonitrile led to o-benzoquinone **11**, while prolonged heating of **9** with 2,2-dimethoxypropane in benzene under reflux furnished cyclic acetal **12**, confirming the vicinal disposition of two hydroxyl groups on aromatic ring.[7]

Other quinols **1b-c** behaved similarly toward acid catalyst to give a mixture of resorcinol diacetate **8b-c** and catechol diacetate **6b-c** in 90-95% yields. The former predominated only slightly over the latter, and ratios of rearranged products **6**/**8** were nearly the same in every case examined.

The mechanism of the quinol-to-catechol rearrangement remains to be clarified. One possible explanation is depicted in Scheme 1; in acid solution quinol acetate **3** is acetylated to form benzenium ion **4**, in which acetoxyl group undergoes 1,3- and 1,2-migration to give isomeric ions **5** and **7**, respectively. These ions lose proton to afford **6** and **8**. Ion **5** could be derived from **4** by direct 1,3-transfer[8] or by successive 1,2-shifts of acetoxyl group. Presumably, more efficient stabilization by acetoxyl groups and less effective destabilization by perfluoroalkyl group of the cationic intermediate **5**, as compared with those of isomeric ion **7**, would be responsible for the unexpected formation of 4-perfluoroalkylcatechols **6**. Hydroquinone derivatives which should arise from the Wagner-Meerwein type shift of perfluoroalkyl group, could not be detected in the product mixtures. Although perfluoroalkyl groups can exchange their relative positions on aromatic ring through the valence-bond isomerism under photochemical conditions,[9] we are not aware of any reports yet on the 1,2-shift of these groups under acid conditions.



Scheme 2.

Perfluoroalkylquinols 1a-c were prepared by the reaction of perfluoroalkyllithium,[10,11] generated in situ from perfluoroalkyl iodide and methyllithium, with benzoquinone in ether at -78 ℃ and subsequent aqueous work-up. In this reaction only 1,2-addition product 1 was obtained; many attemps to realize 1,4-addition failed.

In summary, we have shown for the first time that 4-perfluoroalkyl-4-quinols can rearrange under acid conditions to furnish 4-perfluoroalkylcatechol derivatives. Our finding provides an interesting exception to the usual expectation that quinols rearrange to resorcinols and/or hydroquinones.

References

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7) Satisfactory elemental analyses and/or exact mass molecular weights were obtained for all new compounds. In all cases, ^{1}H (270 MHz), ^{13}C (67.9 MHz), and ^{19}F (254 MHz) NMR data ($CDCl_3$) were consistent with assigned structures.

Spectral data of selected compounds are as follows.

Compounds **6a**+**8a**: ^{1}H δ=2.28, 2.31, 2.31, 2.31 (4 acetyl CH_3), 7.10 (**8a**-H^2, d, J=2.5 Hz), 7.16 (**8a**-H^6, dd, J=8.9, 2.5 Hz), 7.37 (**6a**-H^6, d, J=8.5 Hz), 7.46 (**6a**-H^3, d, J=2.1 Hz), 7.49 (**6a**-H^5, dd, J=8.5, 2.1 Hz), and 7.61 (**8a**-H^5, d, J=8.9 Hz); ^{13}C δ=19.9, 20.0, 20.0, 20.4 (4 acetyl CH_3), 108.9 (both $\underline{C}F_2CF_3$, tm, J_{CF}=269 Hz), 110.2 ($ArCF_2\underline{C}F_2$, ttt, J_{CF}=265, 40, 31 Hz), 110.4 ($Ar'CF_2\underline{C}F_2$, ttt, J_{CF}=265, 53, 44 Hz), 115.1 ($Ar'\underline{C}F_2$, tt, J_{CF}=257, 32 Hz), 115.5 ($Ar\underline{C}F_2$, tt, J_{CF}=258, 48 Hz), 117.4 (both CF_3, qt, J_{CF}=287, 33 Hz), 118.0 (**8a**-C^4, t, J_{CF}=23 Hz), 118.4 (**8a**-C^2), 119.3 (**8a**-C^6), 122.6 (**6a**-C^3 t, J_{CF}=7 Hz), 124.0 (**6a**-C^6), 125.0 (**6a**-C^5, t, J_{CF}=7 Hz), 126.8 (**6a**-C^4, t, J_{CF}=25 Hz), 129.5 (**8a**-C^5, t, J_{CF}=8 Hz), 142.4 (**6a**-C^2), 145.3 (**6a**-C^1, t, J_{CF}=2 Hz), 149.6 (**8a**-C^3, t, J_{CF}=3 Hz), 154.0 (**8a**-C^4, t, J_{CF}=1 Hz), 167.4, 167.5, 168.0, and 168.2 (4 acetyl CO); ^{19}F δ=-81.46 (**8a**-3F, tt, J=10, 2 Hz), -81.53 (**6a**-3F, tt, J=10, 3 Hz), -108.74 (**8a**-2F, m), -110.75 (**6a**-2f, m), -122.42 (**8a**-2F, m), -122.77 (**6a**-2F, m), -125.90 (**6a**-2F, m), and -126.26 (**8a**-2F, m); IR (neat) 1784 (vs), 1426 (s), 1374 (s), 1354 (s), 1192 (vs), 1134 (vs), and 1016 cm^{-1} (m).

Compound **9**: ^{1}H δ=3.35 (6H, s), 6.2 (2H, br-s), 6.88 (1H, d, J=8.5 Hz), 7.06 (1H, d, J=8.5 Hz), and 7.16 (1H, s); ^{13}C δ=50.7, 99.6 (t, J_{CF}=21 Hz), 114.9, 116.0, 122.0, 126.4, 142.9, and 144.7; ^{19}F δ=-81.48 (3F, t, J=10 Hz), -117.77 (2F, m), and -125.22 (2F, m); IR (neat) 3392 (vs), 1614 (s), 1526 (s), 1442 (s), 1344 (s), 1290 (vs), 1234 (vs), 1118 (vs), and 1072 cm^{-1} (vs).

Compound **10**: ^{1}H δ=3.48 (6H, s), 6.44 (2H, m), 7.13 (1H, d, J=9.5 Hz), 7.23 (1H, s), and 8.58 (1H, s); ^{13}C δ=51.0, 103.1 (t, J_{CF}=22 Hz), 104.3, 107.8, 108.1, 131.1, 158.0, and 158.8; ^{19}F δ=-81.32 (3F, t, J=12 Hz), -118.04 (2F, m), and -125.72 (2F, m); IR (neat) 3408 (vs), 1630 (s), 1602 (s), 1514 (s), 1476 (s), 1346 (s), 1228 (vs), 1150 (vs), 1124 (vs), and 1058 cm^{-1} (vs).

Compound **11**: ^{1}H δ=3.48 (6H, t, J_{HF}=1.4 Hz), 6.42 (1H, d, J=10.4 Hz), 6.70 (1H, d, J=2.1 Hz), and 7.24 (1H, dd, J=10.4, 2.1 Hz); ^{13}C δ=51.3, 98.5 (t, J_{CF}=22 Hz), 129.4, 131.7, 138.1 (m), 146.1, 179.26, and 179.3; ^{19}F δ=-81.17 (3F, t, J=11Hz), -117.07 (2F, m), and -124.99 (2F,m); IR (neat) 1694 (s), 1674 (vs), 1402 (s), 1346 (s), 1228 (vs), 1128 (vs), 1084 (vs), and 996 cm^{-1} (vs).

Compound **12**: ^{1}H δ=1.68 (6H, s), 3.38 (3H, t, J=1.5 Hz), 6.71 (1H, d, J=8.2 Hz), 6.96 (1H, s), 7.04 (1H, d, J=8.2 Hz); ^{13}C δ=25.8, 50.8, 99.8 (t, J_{CF}=20 Hz), 107.4, 108.8, 118.4, 122.2, 126.5, 147.3, and 148.3; ^{19}F δ=-81.37 (3F, t, J=11Hz), -117.96 (2F, m), and -125.22 (2F, m); IR (neat) 1496 (s), 1444 (s), 1380 (s), 1342 (s), 1258 (vs), 1230 (vs), 1122 (vs), and 1076 (s).

In ^{13}C-NMR spectra of **9**-**12**, perfluoroalkyl carbons could not be assigned.

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