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Reactions of Perfluoro-2,5-dimethyl-3,4-hexanedione with Amines

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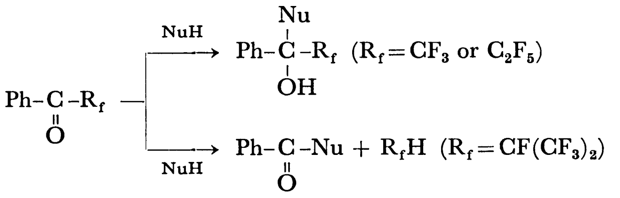
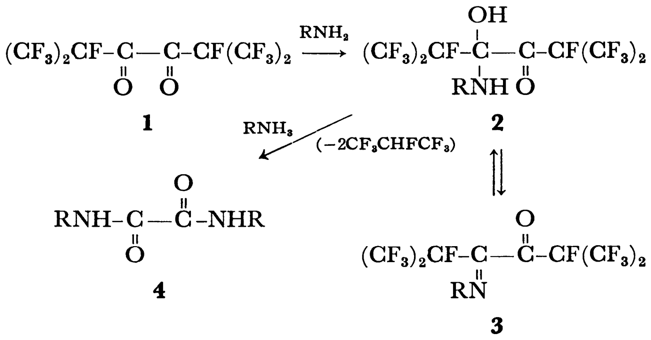
Synopsis. Perfluoro-2,5-dimethyl-3,4-hexanedione and aromatic or aliphatic amines gave the respective 1: 1 adducts in good yields. With excess amounts of aliphatic amines or basic aromatic amines such as *p*-anisidine, the perfluorodiketone gave oxamides. With *o*-phenylenediamine, it gave 2,3-dihydroxyquinoxaline.

In an earlier communication,[1] we reported on the nucleophilic reactions of heptafluoro-1-methylethyl phenyl ketone, which resulted in the formation of benzoic acid derivatives and heptafluoropropane. This made a contrast to trifluoromethyl and pentafluoroethyl phenyl ketones, which are known to form 1: 1 adducts with nucleophiles.



The above fact reveals the enhanced leaving ability of the heptafluoro-1-methylethyl group. This characteristic is presumably ascribable to the high stability of the heptafluoro-1-methylethanide anion as a leaving group and to the bulkiness of that group as a substituent. In this paper we wish to report on similar reactions of perfluoro-2,5-dimethyl-3,4-hexanedione, **1**, an α-diketone carrying two heptafluoro-1-methylethyl groups on both sides.

The reaction of **1** with an equimolar amount of aniline in diethyl ether easily gave a 1: 1 adduct, **2** (R=Ph). When a solution of this adduct in chloroform was heated, a dehydrated product, an imine, **3**, was formed; this substance is, however, very hygroscopic and is readily reconverted into **2**.



Other aromatic amines, such as *p*-toluidine, *p*-chloroaniline, *p*-anisidine, and α-naphthylamine, as well as aliphatic amines, such as butylamine and benzylamine, all gave the corresponding 1: 1 adducts (Table 1).

Whereas perfluorobiacetyl is known to form both 1: 1 and 2: 1 adducts with nucleophiles,[2] **1** did not give a 2: 1 adduct even when an excess of aniline was used. With more basic aromatic amines, however, it gave oxamides, **4**, by releasing two molecules of heptafluoropropane. For example, when 3.3 equivalents of *p*-anisidine were allowed to react with **1** at room temperature for 48 h, *N*,*N*′-bis(*p*-methoxyphenyl)oxamide was obtained quantitatively.

While neither bis(heptafluoro-1-methylethyl) ketone[3] nor heptafluoro-1-methylethyl phenyl ketone[1] forms an addition product such as hydrate or hemiacetal, probably because of their steric effect, **1** is enough released from that effect, as is shown above. The addition of the additional molecule of the amines to the carbonyl group

TABLE 1. PREPARATION AND PROPERTIES OF 1: 1-ADDUCTS (**2**)

	Preparation				Properties of **2**								
R-NH_2	Mole ratio of RNH_2/1	Time (h)	Yield (%)	Mp (°C)	IR (cm^{-1})			^{19}F NMR (δ ppm)[a]			Found (Calcd) (%)		
					NH	OH	C=O	CF_3	CF_3	CF	C	H	N
$PhNH_2$	1.0 2.0	3 3	93 97	133—134	3390	3150—3250	1710	−9.75	−7.80	+95.7	34.72 (34.52)	1.39 (1.45)	2.80 (2.88)
p-$MeC_6H_4NH_2$	1.0	1.5	100	127.5—128	3390	3150—3250	1710	−9.90	−7.80	+95.4	36.24 (35.94)	1.56 (1.81)	2.90 (2.79)
p-$ClC_6H_4NH_2$	2.2	5.5	81	123—124	3390	3300—3400	1720	−9.90	−7.80	+95.4	32.17 (32.24)	1.24 (1.16)	2.70 (2.69)
p-$MeOC_6H_4NH_2$	1.0	0.75	100	127 (dec)	3390	3150—3250	1710	−9.50	−7.70	+95.6	35.08 (34.83)	1.69 (1.75)	2.68 (2.70)
α-$C_{10}H_7NH_2$	2.2	3	90	139 (dec)	3380	3200—3300	1710	−10.20	−8.30	+94.7	40.38 (40.24)	1.70 (1.69)	2.60 (2.61)
n-$BuNH_2$	1.0	2	88	69.5—70.0	3435	3200—3300	1700	−11.25	−8.25	+95.1	30.94 (30.85)	2.56 (2.37)	3.14 (3.00)
$PhCH_2NH_2$	1.0	1	79	91—93	3400	3150—3250	1700	−9.90	−7.95	+94.8	35.83 (35.95)	1.67 (1.81)	3.02 (2.99)

a) The chemical shifts are given in δ ppm upfield from ext. CF_3CO_2H.

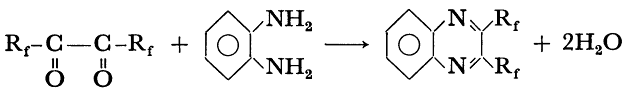
of **2**, however, brought about C–C bond cleavage to afford oxamides. Naturally, aliphatic amines, such as methyl, butyl and benzylamines, reacted much faster than aromatic amines, and when an excess amount was used, they gave oxamides directly (Table 2).

Table 2. Preparation of oxamides, **4**

RNH_2	Mole ratio of $\text{RNH}_2/\mathbf{1}$	Time (h)	Yield[a] (%)	Mp (°C)
$p\text{-MeOC}_6\text{H}_4\text{NH}_2$	3.3	48	100	256—257
MeNH_2	large excess[b]	2	86	215—217
$n\text{-BuNH}_2$	2.2	2	84	152—154
PhCH_2NH_2	2.2	2	100	220—221

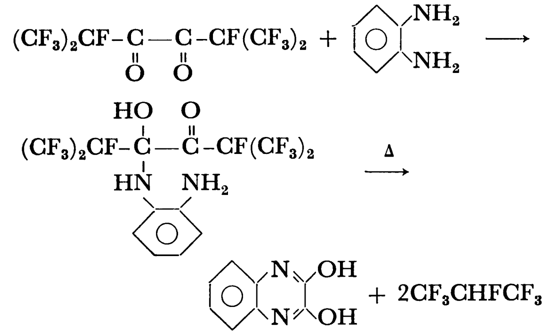
a) All the products were identified with authentic compounds by a comparison of the mps and IR spectra.
b) Methylamine gas was bubbled into an ethereal solution of **1**.

A similar reactivity of the perfluoro diketone **1** was also observed in the cyclization reaction with *o*-phenylenediamine. Perfluorobiacetyl[2] and perfluorooctane-4,5-dione[4] are known to react with *o*-phenylenediamine to give 2,3-bis(perfluoroalkyl)quinoxalines.



$R_f = CF_3$ or $n\text{-}C_3F_7$

In contrast to these diones, we found that the reaction between **1** and *o*-phenylenediamine provides a 1 : 1 adduct, which is then converted into 2,3-dihydroxyquinoxaline by heating in a solvent.



This result indicates again the leaving ability of the heptafluoro-1-methylethyl group as an anion, characterizing the reaction mode of heptafluoro-1-methylethyl ketones.

Experimental

Perfluoro-2,5-dimethyl-3,4-hexanedione (1). This compound was prepared by a modification of the method of Smith *et al.*[3] They made hexafluoropropene to react directly with oxalyl difluoride, which had been prepared from oxalyl dichloride. The difluoride, however, is a poisonous gas and can not be handled safely. Therefore, we used oxalyl dichloride as the starting material and made the difluoride generate *in situ.* Oxalyl dichloride (7.4 g, 58.3 mmol), finely ground dry potassium fluoride (33.8 g, 583 mmol), and acetonitrile (60 ml) were put into a glass tube vessel equipped with a mechanical stirrer. Liquefied hexafluoropropene (175 mmol) was added to the vessel at −70 °C. After having been sealed, the vessel was brought to room temperature. The whole was then heated for 9 h under mechanical stirring in an oil bath kept at 75—80 °C. Thereafter, the lower layer of the reaction contents was separated and subjected to distillation to give **1** (6.0 g, 26%) (bp 91—93 °C) and bis(perfluoro-1-methylethyl) ketone (4.3 g, 20%) (bp 72—73 °C).

Reaction of the Perfluoro Diketone 1 with Aniline. A solution of aniline (0.12 g, 1.3 mmol) in diethyl ether (1 ml) was added, drop by drop, to the diketone **1** (0.5 g, 1.3 mmol) at 0 °C. After 3 h of stirring at room temperature, the crystals which had come out were collected, giving the 1 : 1 adduct **2** (R=Ph) (0.57 g, 93%). Recrystallization from chloroform afforded the pure material (mp 133—134 °C). Reactions with other aromatic amines were carried out in similar manners.

Reaction of 1 with Excess Butylamine. A solution of butylamine (0.16 g, 2.2 mmol) in diethyl ether (4 ml) was added, drop by drop, to perfluoro diketone **1** (0.4 g, 1.0 mmol) at 0 °C. After 2 h of stirring at room temperature, the separated crystals were collected to give *N,N′*-dibutyloxamide (0.17 g, 85%), **4** (R=*n*-Bu). Reactions with other amines to give oxamides, **4**, were carried out in similar manners. The products thus obtained were identified with the authentic samples by a comparison of the melting points and IR spectra.

Reaction of 1 with o-Phenylenediamine. A solution of *o*-phenylenediamine (0.076 g, 0.7 mmol) in acetonitrile (0.5 ml) was added to perfluoro diketone **1** (0.25 g, 0.64 mmol) at 0 °C. After 30 min of stirring at room temperature, it was filtered to give a 1 : 1 adduct (0.27 g, 85%) (mp >300 °C). IR: 3400—3500 (OH), 3350, 3300 (NH), 1705 (C=O) cm^{-1}.

A solution of the 1 : 1 adduct in ethanol was refluxed for 1 h, and the separated crystals were collected to give 2,3-dihydroxyquinoxaline (mp >300 °C), in an 84% yield. This product was identified with an authentic sample by means of its IR spectrum.

References

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