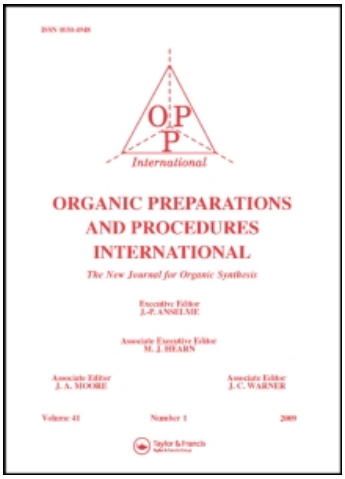

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N-PERFLUOROALKANESULFONYLPHOSPHORAMIDES

via AN IMPROVED ATHERTON-TODD REACTION

Submitted by
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Phosphoramides have received much attention due to their biological properties;[1] for example, sulfonyl phosphoramides are important pesticides.[2] It is well known that the introduction of a fluorine atom or fluorine-containing group into organic molecules often increases their chemical or biological activities. Therefore it might be valuable to develop synthetic methods for the preparation of fluorine-containing phosphoramides and their derivatives. We recently prepared the N-perfluoroalkanesulfonylphosphoramides ($R_fSO_2N(R)P(O)(OR')_2$) by two different methods. The first involved the reaction of perfluoroalkanesulfonyl azides with triethyl phosphite, to give $R_fSO_2N{=}P(OEt)_3$ which readily rearranges to $R_fSO_2N(Et)P(O)(OEt)_2$, albeit in a yield of only about

$$R_fSO_2N_3 + P(OEt)_3 \longrightarrow R_fSO_2N{=}P(OEt)_3 \longrightarrow R_fSO_2N(Et)P(O)(OEt)_2 \quad (1)$$

40% (Eq. 1)[3] and the second method uses the Arbuzov reaction (Eq. 2).[4] This paper reports a new convenient method to prepare the title compounds.

$$R_fSO_2N(R')X + P(OR)_3 \longrightarrow R_fSO_2N(R')P(O)(OR)_2 + R'X \quad (2)$$

X = Cl, Br

The phosphorylation of perfluoroalkanesulfonylamides (**1**) was carried out with dialkyl phosphites (**2**) in carbon tetrachloride under basic reaction conditions and in the presence of a small amount of a phase-transfer catalyst, hexadecyltributylphosphonium bromide (Eq. 3).

$$R_fSO_2NHR \quad + \quad (R'O)_2P(O)H \xrightarrow[\text{cat., RT}]{KOH/CCl_4} R_fSO_2N(R)P(O)(OR')_2 \qquad (3)$$

1 2 3

Cat.: $CH_3(CH_2)_{15}\overset{+}{P}(C_4H_9)_3 \ Br^-$

This reaction proceeds easily at room temperature. After work-up, the products were purified by vacuum distillation. All products **(3)** are high boiling oils. The data show that the phosphorylation of the primary perfluoroalkanesulfonylamides proceeded in good yields (Table 1). Attempts to use organic bases such as triethylamine or pyridine instead of potassium hydroxide or to perform the reaction without the phase-transfer catalyst, failed to give the expected products **(3)**.

In summary, this procedure for the phosphorylation of perfluoroalkanesulfonylamides appears to be a practical method for the preparation of the title compounds by the Atherton-Todd reaction.[5]

Table 1. Compounds **(3)** prepared

	Substrate **1**		Substrate **2**	Products	bp. (°C / Torr)	Yield
	R_f	R	R'			(%)
1a	CF_3	H	Et	**3a**	115-118 / 0.03	78
1b	C_4F_9	H	Et	**3b**	120-123 / 0.03	75
1c	C_4F_9	Et	Et	**3c**	160 / 1	69
1d	$I(CF_2)_2O(CF_2)_2$	Me	Et	**3d**[a]	204 / 1	67
1e	$I(CF_2)_2O(CF_2)_2$	Et	Et	**3e**	210 / 1	65
1f	$H(CF_2)_2O(CF_2)_2$	Me	Et	**3f**[a]	180 / 1	60
1g	$H(CF_2)_2O(CF_2)_2$	Et	Et	**3g**	190 / 1	64

a) Identified by comparison with authentic samples.[4]

EXPERIMENTAL SECTION

Bps were reported uncorrected. ^1H NMR (60MHz) and ^{19}F NMR (54.6 MHz) spectra were recorded on a Varian 360L instrument using TMS and TFA as internal and/or external standards respectively. IR spectra were obtained on a IR-440 Shimadzu spectrophotometer. Low resolution mass spectra were recorded on a Finnigan GC-MS 4021 instrument. Elemental analyses were performed by the Analysis Department of this Institute. Compound **(1a)** was prepared by the reaction of $(CF_3SO_2)_2O$ with NH_3 at -60°. The other compounds **(1)** were prepared from R_fSO_2F according to the literature method.[4]

Preparation of Compounds (3). Typical Procedure.- Diethyl phosphite **(2)** (0.83g, 6.0 mmol) was added dropwise into a 25 mL flask containing a CCl_4 solution (3 mL) of $CF_3SO_2NH_2$ **(1a)** (0.75g, 5.0mmol), KOH (0.5g) and hexadecyltributylphosphonium bromide (0.1g). The reaction mixture was stirred for 8h at room temperature. After filtration to remove the solid and evaporation of the solvent, the residue was distilled under vacuum to give pure **3a** for analysis.

TABLE 2. Spectra Data of Compounds **3a-3g**

Cmpd	IR (film, cm^{-1})	^1H NMR (ppm)	^{19}F NMR (ppm)	MS (m/z, %)	Analysis (Found)
$CF_3SO_2NHP(O)(Oet)_2$ (**3a**)	3357 (s, NH) 1394 (s ,S=O) 1238 (s, P=O)	10.40 (s, 1H) 4.20 (m, 4H) 1.35 (t, 6H)	2.4 (s, CF_3).	286 (M^++1, 5.1), 160 ($^+SO_2NHP(O)(OH)_2$, 100).	C, 21.05 (21.17) H, 3.86 (4.01) N, 4.91 (4.77)
$C_4F_9SO_2NHP(O)(OEt)_2$ (**3b**)	3378 (s, NH) 1397 (s, S=O) 1237 (s, P=O) 1210-1120 (vs, C-F), 1135 (s).	9.96 (s, 1H) 4.18 (m, 4H) 1.36 (m, 6H)	3.4 (s, CF_3), 34.2 (m, CF_2) 45.8 (m, CF_2) 52.3 (s, CF_2S).	436 (M^++1,7.90), 160 ($^+SO_2NHP(O)(OH)_2$, 100).	C, 22.07 (21.92) H, 2.53 (2.60) N, 3.22 (3.05)
$C_4F_9SO_2N(Et)P(O)(OEt)_2$ (**3c**)	2980 (s) 1360 (s, S=O) 1245 (s, P=O) 1220-1130 (vs, C-F), 1135 (s)	3.74 (m, 4H) 3.25 (m, 2H) 0.87 (m, 9H).	4.7 (s, CF_3) 37.0 (m, CF_2) 44.8 (m, CF_2) 51.9 (s, CF_2S).	464 (M^++1, 1.4) 99 ($^+NH_2P(OH)_2H$, 100).	C, 25.92 (26.11) H, 3.42 (3.52) N, 3.02 (3.22)
$I(CF_2)_2O(CF_2)_2SO_2N(Me)P(O)(OEt)_2$ (**3d**)	3350 (m), 1400 (m), 1330, 1290 (s, S=O) 1230 (s, P=O), 1200-1120 (vs, C-F),1020 (s).	3.98 (m, 4H) 2.93 (d, $^3J_{HP}$= 10.4Hz, 3H) 1.04 (m, 6H).	-8.8 (s, ICF_2) 5.6 (m, OCF_2) 9.21 (m, CF_2O) 36.7 (s, CF_2S).	574 (M^++1, 1.7) 174 ($^+SO_2N(Me)P(O)(OH)_2$, 100).	/
$I(CF_2)_2O(CF_2)_2SO_2N(Et)P(O)(OEt)_2$ (**3e**)	3000 (m), 1440 (m), 1390, 1280 (s, S=O), 1235 (s, P=O), 1200-1100 (vs, C-F) 1020 (s)	4.08 (m, 4H) 3.37 (m, 2H) 1.24 (m, 9H).	-7.7 (s, ICF_2) 3.6 (m, OCF_2) 9.3 (m, CF_2O) 35.7 (s, CF_2S).	588 (M^++1, 1.7) 108 ($^+SO_2NHEt$, 100)	C, 20.44 (20.32) H, 2.56 (2.71) N, 2.39 (2.14)
$H(CF_2)_2O(CF_2)_2SO_2N(Me)P(O)(OEt)_2$ (**3f**)	2990, 2930 (m) 1440 (w) 1400 (s), 1320, 1280 (s, S=O) 1240 (s, P=O) 1230-1120 (vs, C-F), 1030 (s)	5.85 (t, $^2J_{HF}$= 54.0Hz, HCF_2) 3.80 (m, 4H) 2.71 (d, $^3J_{HP}$= 10.4Hz, 3H) 0.94 (m, 6H).	4.3 (m, OCF_2) 10.8 (m, CF_2O) 38.1 (s, CF_2S) 61.9 (d, HCF_2).	448 (M^++1, 19.54) 174 ($^+SO_2N(Me)P(O)(OH)_2$, 100)	/
$H(CF_2)_2O(CF_2)_2SO_2N(Et)P(O)(OEt)_2$ (**3g**)	3000 (m), 2920 (m), 1440 (w), 1400 (s), 1320, 1280 (s, S=O) 1233 (s, P=O), 1230-1110 (vs, C-F).	5.83 (t, $^2J_{HF}$= 54.0Hz, HCF_2) 3.81 (m, 4H) 3.12 (m, 2H) 0.93 (m, 9H)	4.3 (m, OCF_2) 10.7 (m, CF_2O) 38.6 (s, CF_2S) 61.8 (d, HCF_2).	461 (M^+, 2.80) 188 ($^+SO_2N(Et)P(O)(OH)_2$, 100).	C, 26.03 (25.98) H, 3.47 (3.41) N, 3.04 (3.07)

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A NOVEL SYNTHESIS OF 4-CYANO-2-(2-HYDROXYBENZOYL)PYRIDO[1,2-*a*]-BENZIMIDAZOLES FROM 3-FORMYLCHROMONE

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A number of pyrido[1,2-*a*] benzimidazole derivatives have been reported to have interesting biological properties like analgesic and antiinflammatory[1], antiviral[2], antimicrobial[3] and antineoplastic[4] activities. Other pyrido [1,2-*a*] benzimidazole derivatives possess the fluorescent properties and are used in synthetic fibers[5]. In continuation of our work of elaborating 3-formylchromones (**1**)[6] into a variety of fused heterocyclic systems[7] of biological interest, we herein report a novel, single step synthesis of pyrido [1,2-*a*]benzimidazoles starting from the readily available synthon **1**.

Thermal condensation of **1** with 1H-benzimidazole-2-acetonitrile **2**[8] in ethylene glycol at 200-210° gave a compound, homogeneous by TLC mp. 250-252°, in 70% yield. Its IR spectrum shows the presence of -OH(3065cm^{-1}), -CN(2235cm^{-1}) and -CO(1645cm^{-1}). Based on the above data, its ^{1}H NMR and MS (m/e 313), the structure of this compound was readily assigned as 4-cyano-2-(2-hydroxybenzoyl)pyrido[1,2-*a*]benzimidazole **4** as shown below.