CATALYTIC HYDROFORMAMINATION OF 2,5-DIMETHOXY-2,5-DIHYDROFURANS

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N-Substituted 3- and 4-formylpyrroles have been obtained by hydroformamination of 2,5-dimethoxy-2,5-dihydrofurans in the presence of $HRh(CO)(PPh_3)_3$.

Hydroformamination (HF) of 2,3- and 2,5-dihydrofurans has been reported to give 3-alkylimino(amino)methyltetrahydrofurans [1].

We have now examined the HF of 2,5-dimethoxy-2,5-dihydrofurans (I) in the presence of primary amines and the homogeneous rhodium complex catalyst $RhH(CO)(PPh_3)_3$. It has been found that HF of (Ia) affords the 3-formylpyrroles (IIa)-(Va), while in the case of 2-methyl-2,5-dimethoxy-2,5-dihydrofuran (Ib), the 2-methyl-4-formylpyrroles (IIb)-(IVb) are formed selectively:



The IR spectra of (II)-(IV) show characteristic carbonyl absorption (Table 1) at 1670-1675 cm⁻¹, and for the pyrrole ring at 1500-1615 cm⁻¹. The absorption seen in the UV region is characteristic of pyrroles with an electronegative substituent in the β -position [2].

Compound	Yield, %	Bp, °C (p, mm Hg)	n_{D}^{22}	IR spec- trum, \vee , cm ⁻¹	UV spectrum in ethanol, λ_{max} , nm (ϵ)
(IIa)	47	114-117(4)	1,5411	1670 1535 1610	310 (2300) 270 (13200) 245 (18300)
(IIIa)	63	123-125(3)	1,5238	1670 1535 1615	340 (450) 281 (15400) 257 (14500)
(IVa)	57	149–150 (3)	1,6265	1675 1510 1540 1600	269 (22800) 229 (15100) 200 (29600)
(IIb)	51	156-158(8)	1,4586	1670 1535 1615	286 (7600) 255 (1400) 207 (16600)
(IIIÞ)	74	132–133(3)	1,5245	1675 1530 1570	290 (9200) 256 (18400) 208 (21600)
(IVb)	48	170–172(3)	1.6153	1670 1500 1525 1600	255 (2340 0) 200 (3 0000)

TABLE 1. Physicochemical and Spectral Data for (II)-(IV)

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Com- pound	Ηα	Ħ ^β	-CH=0	\mathbf{R}^1	R²
(IIa) (IIIa)	$\begin{array}{c} 6,60 \text{ d.d. q} \\ (3,0,2,0,0,7) \\ 6,65 \text{ d.d} \\ (2,9,2,0) \end{array}$	6,53 d.d.d. (3,0, 2,0, 0,8) 6,58 d.d (2,9, 1,8)	9,67 d (0,8) 9,71 s	7,18 d.d (2,0, 2,0) 7,27 d.d (1,8, 2,0)	3,65 d (0,7) 3,90 t (7,3) 1,76 quint (7,3) 1,32 q.t (7,3, 7,3) 0,91 t (7,3)
(IVa)	6,93 d.d (3,1, 2,1)	6.65 d.d (3,1, 1,7)	9,69 s	7,53 d.d (1,7, 2,1)	7,10 - 7,40 m
(IIb)	7,11 d.d (1,8, 0,6)	6,23 d.q.d (1,8, 1,0, 0,4)	9,54 d (0,4)	2,12 d (1,0)	3,49 d (0,6)
(IIID)	7,19d (1,9)	6,3d.q.d (1,9, 1,0, 0,5)	9,63 d (0,5)	2,19 đ (1,0)	3,81t (7,5), 1,68.9 (7,5) 1.32 9.t (7,5, 7,5)
(IVb)	7,22 d (2,0)	6,39d.q.d (2,0, 1,0, 0,5)	9,64 d (0,5)	2,02 đ (1,0)	7,10-7,50 m

TABLE 2. ¹H NMR Spectra of N-Substituted Pyrroles (δ , ppm; CDCl₃; J, Hz)

the structures of (II)-(IV) were proved by their ¹H and ¹³C NMR spectra (Tables 2 and 3). Specifically, the PMR spectra of (II)-(IV) contain signals with chemical shifts of 9.54-9.71 ppm, indicating the presence of a formyl group attached to a pyrrole ring carbon. The ring β -protons appear in the spectra as signals with chemical shifts of 6.23-6.39 ppm (IIb)-(IVb) and 6.53-6.65 ppm (IIa)-(IVa). The location of the substituents in the pyrrole ring is also shown by the ¹H-¹H coupling constants through differing numbers of bonds. Thus, ³J_H⁴-H⁵ = 2.9-3.1, ⁴J_H⁴-H² = 1.7-2.0, ⁴J_H²-H⁵ = 2.0-2.1, and ⁴J_H³-H⁵ = 1.8-2.0 Hz. Similar ¹H-¹H coupling constants have been reported [3] for di- and trisubstituted pyrroles.

The doublets with chemical shifts of 184.58-185.39 ppm and ${}^{1}J_{C-H} = 168.1-170.5$ Hz seen in the ${}^{13}C$ NMR spectra are assigned to the carbon atom of the formyl group. The signals with chemical shifts of 105.50-109.47 ppm and direct coupling constants of 170.6-174.5 Hz indicate the presence of substituent-free fourth (IIa)-(IVa) and third (IIb)-(IVb) positions of the pyrrole ring, respectively. The signals for C³ and C⁴ with the formyl substituent were assigned using the geminal ${}^{13}C^{-1}H$ coupling constants, the values of which were 23.7-24.4 Hz and were measured by selective transfer of polarization (SPI) from the formyl hydrogen atom [4]. The signals for C² and C⁵ were assigned by comparison of the vicinal coupling constants ${}^{3}J = 2.6-3.1$ Hz with the literature values for N-substituted five-membered nitrogen heterocycles [5].

EXPERIMENTAL

Hydroformaminations were carried out in a rotary stainless steel (Kh18N10T) autoclave of capacity 0.15 liter. The autoclave was placed in an electrically heated furnace. The reaction was carried out at 100°C at an initial pressure of the CO and H₂ mixture of 100 atm $(CO:H_2 = 1:1, molar)$. The catalyst and (Ia, b) were obtained as described in [6, 7]. The autoclave was charged with 0.01 mmole (0.1032 g) of RhH(CO)(PPh₃)₃, 0.035 mole of freshlydistilled (I), 0.035 mole of the primary amine, and 35 ml of dry benzene. The reaction times were 1.5-2 h. The catalyzate was then submitted to fractional distillation, and the reaction products analyzed on a Chrom-4 chromatograph with a flame ionization detector, a 5 mm × 100 mm stainless steel column with 5% SE-30 on Chromatone N-AW, evaporator temperature 300°C, carrier gas helium, 25 ml/min; the column temperature ranged from 120 to 200°C.

IR spectra were obtained on a UR-20 apparatus in thin films on KBr. The UV spectra of ethanolic solutions were obtained on a Specord UV-VIS spectrophotometer.

¹H NMR spectra were recorded on a Bruker WM-250, operating frequency for protons 250.13 MHz, and ¹³C NMR spectra on an AM-300, operating frequency 75.47 MHz, relative to TMS as internal standard.

The signals in the ¹H and ¹³C NMR spectra were assigned by selective homo-¹H-{¹H} and heteronuclear ¹³C-{¹H} resonance.

Other atoms		121,0, 127,27, 129,80, 139,43	13,49, 19,67 32,72, 46,96	125,28, 127,84, 129,00, 138,35	
о С—Н	185,02 d (169,0)	185, 39 d (170,5)	184,78 d (168,2)	184,84 d (168,1)	184,58đ (169,1)
CH3	36,499 (139,3)	11,70° q	(127,7) 34,17 q (138,4)	11,81 q (128,0)	12,239 (128,0)
ů	124,30 d.d.d.q (183,0, 3,3, 3,3, 3,0)	122,24 d.d.d (189,2, 7,1, 7,7)	130.44 d.q.d (184,8, 7,6, 3,0)	129,23 d.d.t (182,4, 5,4, 3,1)	129,96 d.d (187,4, 6,3)
õ	108,05 d.d.d.d.d.	109,47 d.d.d.d.d.	124,98 d.d.d (23,7, 6,6, 3,1)	125,14 d.d.d (24,0, 6,2, 3,4)	125,89 d.d.d (24,4, 3,4, 6,3)
ບົ	126,50 d.d.d.d.d (24,0, 10,8, 7,3, 3,8)	128,10 d.d.d.d.d.	105,50 d. d. d. q (172,6, 4,5, 4,0, 3,8)	105,80 d.d.d.q (170,6, 5,6, 3,8, 4,0)	106,05 d. d. d. q (172,5, 5,8, 4,0, 3,8)
రి	129,96 d. d. d. q (182,0, 6,5, 6,2, 3,0)	127,14d.d.d (184,2, 6,6, 5, 3)	132,00 q.q.d (6,4, 5,0, 3,0)	131,42 q.t.d (6,8, 2,6, 5,3)	131,87 d.q (6.0, 6,8)
Compound	(11a)	(111a)	(IVa)	(qII)	(4/1)

 $^{13}\mathrm{C}$ NMR Spectra of N-Substituted Pyrroles (6, ppm; CDCl_3; J, Hz) TABLE 3.

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ELECTROCHEMICAL SYNTHESIS OF PERFLUOROALKYLCHLORIDES

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Electrooxidation of perfluorocarboxylic acids in the presence of Cl_2 yields perfluoroalkylchlorides R_FCl . It is suggested that anodic oxidation of perfluorocarboxylate ions is the determining electrochemical stage in this electrochemical version of the Borodin-Hundsdikker reaction.

It has been established [1] that CF_3I (I) is formed during electrooxidation of I_2 in a CF_3COOH medium. According to the scheme proposed, an iodine cation I⁺ interacts with CF_3COOH to produce trifluoroacetylhypoiodite, which breaks down to form (I). The suggestion of intermediate formation of an acylhypoiodite is similar to the scheme proposed from a traditional standpoint for the mechanism of the Borodin-Hundsdikker reaction [2].

The yield of (I) was not indicated so that it is not possible to estimate the preparative value of the reaction. An electrochemical version of the Borodin-Hundsdikker reaction has been used successfully for synthesis of CF_3Br (II): electrolysis of CF_3COOH in anhydrous MeCN in the presence of Br_2 on a Pt anode produced (II) with a material yield (MY) of 70% [3]. The use of similar reactions for synthesis of perfluoroalkylchlorides has so far not been described.

We have found that electrolysis of perfluorocarboxylic acids $R_FCOOH(III)$ [$R_F = CF_3$, C_8F_{17} , $FSO_2CF_2CF_2OCFCF_3$, $FSO_2CF_2CF_2OCF(CF_3)CF_2OCFCF_3$, $H(CF_2CF_2)_3$] and Cl_2 on a Pt anode at a potential of +2.6 V and a current density of 50 mA/cm² in aqueous MeCN leads to formation of the corresponding perfluoroalkylchlorides with a material yield of 55-94% and a yield with respect to current (CY) of 21-54%. Competing reactions which occur to a slight extent are formation of Kolbe dimers and reaction of electrochemically generated perfluoroalkyl radicals with the solvent.

Figure 1 shows polarization curves of a platinum electrode in a water-acetonitrile solution (1:1) of trifluoroacetate acidified with CF_3COOH . It is clear that appreciable discharge of the CF_3COO^- anion (curve 1) starts at potentials >2.5 V. Analysis of the products of electrolysis carried out at these potentials shows that the main product is hexafluoroethane with traces of fluoroform. When the solution is saturated with gaseous chlorine, curve 2 shows an oxidation wave for chloride ions (with a maximum at a potential of 1.4 V), which result from chemical reactions of chlorine with the solvent:

$$2\mathrm{Cl}^{-} - 2e \to \mathrm{Cl}_{2} \tag{1}$$

$$Cl_2 + CH_3CN \rightarrow ClCH_2CN + HCl$$
 (2)

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