Acylation of 2-methoxypropene with anhydrides and halides of perfluorocarboxylic acids in the presence of tertiary amines

D. V. Gorlov,* M. A. Kurykin, and O. E. Petrova

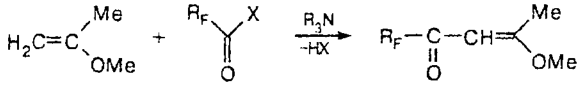
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: mak@ineos.ac.ru

3-Methoxy-1-(perfluoroalkyl)but-2-en-1-ones were synthesized by *C*-acylation of 2-methoxypropene with perfluorocarboxylic acid anhydrides, acid chlorides, and acid fluorides in the presence of tertiary amines.

Key words: *C*-acylation, 2-methoxypropene, methyl propen-2-yl ether, monoacylated polyfluorinated derivatives; perfluorocarboxylic acid anhydrides and halides.

C-Acylation of alkyl vinyl ethers with perhalogenated acid anhydrides was studied with only trifluoro- and trichloroacetic anhydrides as examples.[1—4] It was shown that alkyl vinyl ethers can undergo, depending on the reaction conditions, either mono-[2] or diacylation.[3] 2-Methoxypropene (**1**) is only monoacylated.[4] The structures of the resulting alkyl perhaloacylvinyl ethers allow them to be used for the synthesis of various heterocyclic systems and β-dicarbonyl compounds, in particular, trifluoroacetylacetone homologs containing any perfluorinated radicals. In the present work, the reactions of vinyl ether **1** with other anhydrides and some perfluorocarboxylic acid halides in the presence of tertiary amines were studied.

We established that, under these conditions, vinyl ether **1** is *C*-monoacylated with perfluorocarboxylic acid anhydrides, acid chlorides, and acid fluorides (**2—4**) to give the corresponding 3-methoxy-1-(perfluoroalkyl)but-2-en-1-ones (**5**) in good yields (Table 1) independent of the R_F length.



1 **2—4** **5**

$R_F = CF_3$ (**a**), C_2F_5 (**b**), C_3F_7 (**c**), C_4F_9 (**d**), C_6F_{13} (**e**), C_8F_{17} (**f**);
X = Cl (**2**), F (**3**), $OCOR_F$ (**4**);
R_3N = Py, Et_3N

Note that the *C*-acylation of ether **1** with perfluorocarboxylic acid fluoride **3e** in the presence of pyridine does not result in the expected *C*-monoacylated derivative. However, the use of Et_3N as a base allowed us to obtain the target compound **5e** in a moderate yield. It should also be noted that each of compounds **5a—f** exists as one of two possible geometric isomers, but their configurations were not determined by us.

All the products synthesized are mobile transparent yellowish liquids with a characteristic odor.

Table 1. *C*-Acylation of ether **1** with R_FCOX

Product	X in R_FCOX	Base	Solvent	*T*/°C	Yield (%)	B.p./°C (*p*/Torr)	Found/Calculated (%)		
							C	H	F
5a	Cl	Py	Et_2O	−55	74	68 (20)*	—	—	—
	Cl	Py	CH_2Cl_2	−30	45				
	$OCOCF_3$	Et_3N	CH_2Cl_2	0	74				
5b	$OCOC_2F_5$	Py	CH_2Cl_2	−30	66	162	38.09 38.53	3.31 3.21	43.38 43.58
5c	Cl	Py	CH_2Cl_2	−40	73	170	35.77 35.82	2.75 2.61	50.16 49.63
5d	Cl	Py	CH_2Cl_2	8—20	76	68 (4)	33.88 33.96	2.40 2.20	53.99 53.77
5e	F	Et_3N	Et_2O	−30	45	104 (8)	31.45 31.58	1.58 1.67	60.18 59.09
5f	Cl	Py	CH_2Cl_2	−30	61	97 (3)	29.79 30.11	1.35 1.35	62.71 62.35

* Data from Ref. 1.

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Table 2. ^1H and ^{19}F NMR spectral data for the compounds synthesized

Compound	δ ^1H	δ ^{19}F (*J*/Hz)
5a*	2.40 (s, CH_3); 3.80 (s, OCH_3); 5.70 (s, CH)	2.3 (s, CF_3)
5b	2.60 (s, CH_3); 4.10 (s, OCH_3); 6.10 (s, CH)	6.6 (s, CF_3); 47.5 (s, CF_2)
5c	2.50 (s, CH_3); 3.90 (s, OCH_3); 6.00 (s, CH)	5.2 (t, CF_3); 45.5 (q, CF_2, $J = 9$); 51.0 (s, CF_2)
5d	2.60 (s, CH_3); 4.00 (s, OCH_3): 6.00 (s, CH)	5.8 (t, CF_3, $J = 9$); 44.8 (q, CF_2, $J = 9$); 47.5 (m, CF_2); 50.0 (m, CF_2)
5e	2.30 (s, CH_3); 3.80 (s, OCH_3); 5.80 (s, CH)	6.0 (s, CF_3); 44.7 (m, CF_2); 45.9 (m, CF_2); 46.6 (m, CF_2); 47.1 (m, CF_2); 50.8 (m, CF_2)
5f	2.40 (s, CH_3); 3.80 (s, OCH_3); 5.80 (s, CH)	6.0 (s, CF_3); 44.8 (m, CF_2); 45.6 (m, CF_2); 46.1 (m, 2 CF_2); 46.5 (m, CF_2); 47.0 (m, CF_2); 50.9 (m, CF_2)

* Data from Ref. 1.

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker AC-200F spectrometer (200 and 188.4 MHz, respectively) with Me_4Si (^1H) and CF_3COOH (^{19}F) as the external standards. Elemental analysis of the compounds obtained was performed at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences. The solvents were dried according to the standard procedures.[5]

***C*-Acylation of 2-methoxypropene (1) (general procedure).** An acylating agent **2**—**4** (1 mol) was added dropwise with vigorous stirring at a temperature indicated in Table 1 to a mixture of ether **1** (1 mol) and a tertiary amine (1 mol) in a dehydrated solvent. The reaction mixture was stirred at the same temperature for ~1 h, allowed to be heated gradually to room temperature, and poured into water. The organic layer was separated off, washed with water, and dried over $CaCl_2$. The solvent was removed, and the corresponding compounds **5a**—**f** were isolated by distillation (see Table 1). The ^1H and ^{19}F NMR spectral data of the reaction products are given in Table 2.

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Synthesis of new dialkyl α-aminophosphonates and dialkyl α-aminothiophosphonates

O. A. Aimakov,[a] K. B. Erzhanov,[a] and T. A. Mastryukova[b]*

[a]*Sh. Sh. Ualikhanov Kokshetau University,*
76 ul. K. Marksa, 475003 Kokshetau, Republic of Kazakhstan.
Fax: +7 (316 22) 55 584
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: mastr@ineos.ac.ru

New dialkyl α-aminophosphonates and α-aminothiophosphonates were synthesized by reactions of dialkyl phosphites or *O,O*-dialkyl thiophosphites with *N*-benzylidene-2-(vinyloxy)ethylamine or *N*-(4-fluorobenzylidene)-2-(vinyloxy)ethylamine.

Key words: dialkyl phosphites, *O,O*-dialkyl thiophosphites, reaction with Schiff bases, dialkyl α-aminophosphonates, dialkyl α-aminothiophosphonates, synthesis.

The Kabachnik—Fields reaction is a classic method for the synthesis of α-aminophosphonates and their numerous functionalized derivatives. Synthetic aspects of this reaction have been well developed and discussed in monographs and reviews.[1—4]

However, despite extended investigations in the field of alkyl α-aminophosphonates, condensation of *N*-benzylidene-2-(vinyloxy)ethylamine or *N*-(4-fluorobenzylidene)-2-(vinyloxy)ethylamine with dialkyl phosphites or *O,O*-dialkyl thiophosphites is not reported in the

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