ucts. These results indicate the possibility of an olefin–carbene isomerization of tetrafluoroethylene to trifluoromethylfluorocarbene under these conditions. Hence, the formation of hexafluoropropylene in the thermolysis of tetrafluoroethylene may be the result of the recombination of difluorocarbene with trifluoromethylfluorocarbene.

LITERATURE CITED

1. B. Atkinson and V. A. Atkinson, J. Chem. Soc., 2086 (1957).
2. J. N. Butler, J. Am. Chem. Soc., 84, 1393 (1962).
3. S. F. Politanskii, Kinet. Katal., 10, 500 (1969).
4. S. H. Bauer, K. C. Hou, and E. L. Resler, Phys. Fluids, 12, 125 (1969).
5. V. G. Barabanov, G. V. Volkov, K. A. Vyuonov, and V. N. Maksimov, Zh. Obshch. Khim., 55, 868 (1985).
6. V. G. Barabanov, G. V. Volkov, K. A. Vyuonov, and V. P. Makoveenko, Zh. Obshch. Khim., 56, 1134 (1986).
7. O. M. Nefedov and A. A. Ivashenko, Izv. Akad. Nauk SSSR, Ser. Khim., 446 (1968).
8. G. R. Barnes, R. A. Cox, and R. F. Simmons, J. Chem. Soc., B, 1176 (1971).
9. N. D. Kagramanov, P. S. Zuev, A. A. Kutin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 46 (1989).
10. V. G. Barabanov, L. V. No, M. U. Fedurtsa, and I. D. Kushina, Zh. Obshch. Khim., 54, 824 (1984).

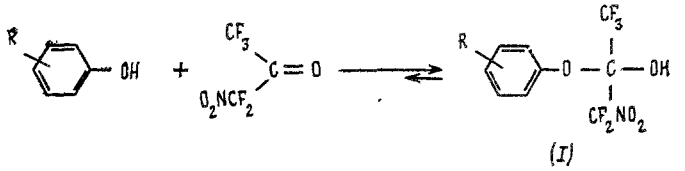
REACTION OF NITROPENTAFLUOROACETONE WITH PHENOLS

V. I. Dyachenko, A. F. Kolomiets, and A. V. Fokin

UDC 542.91:547.447.4'161:547.56:66.095.253

In previous work [1, 2], we examined the uncatalyzed reactions of hexafluoroacetone and methyl trifluoropyruvate with phenols. In the present work, we studied the behavior of nitropentafluoroacetone (NPFA), which is one of the most electrophilic carbonyl compounds [3, 4], in these reactions.

NPFA reacts with phenol, cresols, halophenols, and esters of hydroxybenzoic acids in CCl_4 and $MeNO_2$ at 20°C, as with alcohols [4], to give hemiketals (I), which give ^{13}C NMR signals in the vicinity of 95 ppm characteristic for this type of compounds.

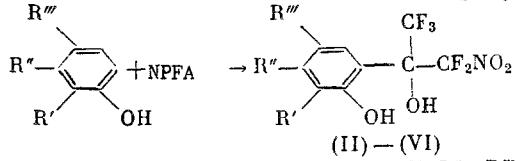


(I)

R=H, CH_3, Hal, $COOCH_3$,

Hemiketals (I) decompose upon fractionation in vacuum to the starting phenol and NPFA.

NPFA reacts with phenols which have a high tendency to undergo electrophilic replacement such as pyrogallol, resorcin derivatives, and 3,4-methylenedihydroxyphenol in these solvents at 20°C to give o-alkylation products (II-(V) in high yields.



(II) – (VI)

R′=R″=OH, R‴=H (II); R′=R‴=H, R″=OCH_3 (III); R′=H, R″=R‴=O–CH_2–O (IV); R′=H, R″=OH, R‴=$C(CF_3)_2OH$ (V), R′=R‴=H, R″=CH_3 (VI).

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1436-1440, June, 1989. Original article submitted October 20, 1988.

0568-5230/89/3806-1315$12.50

© 1989 Plenum Publishing Corporation

TABLE 1. Reaction Conditions, Yields, and Properties of (II)-(VIII)

Compound	Reaction conditions		Yield, %	Mp, °C (solvent)	R_f	Found/Calculated, %				Chemical formula
	time, h	solvent				C	H	N	F	
(II)	12	$MeNO_2$	97,1	93–95 Benzene	0,16	35,12 / 34,95	1,92 / 1,94	4,42 / 4,53	31,15 / 30,74	$C_9H_6NF_5O_6$
(III)	12	CCl_4	99,0	67–69 Hexane	0,36	37,82 / 37,86	2,70 / 2,52	4,40 / 4,42	– / –	$C_{10}H_8NF_5O_5$
(IV)	12	Benzene	90,6	128–130 Benzene	0,35	36,57 / 36,25	1,74 / 1,81	4,15 / 4,23	28,72 / 28,70	$C_{10}H_6NF_5O_6$
(V)	144	$MeNO_2$	99,9	150–152 Benzene	0,24	31,35 / 31,37	1,35 / 1,31	2,85 / 3,05	45,04 / 45,53	$C_{12}H_6NF_{11}O_6$
(VI)	3	CCl_4	36,3	64–66 Hexane	0,46	39,50 / 39,87	2,60 / 2,66	4,44 / 4,65	31,35 / 31,56	$C_{10}H_8NF_5O_4$
(VII)	144	$MeNO_2$	99,7	*	0,57	39,95 / 39,98	3,08 / 3,02	4,38 / 4,23	28,99 / 28,70	$C_{11}H_{10}NF_5O_5$
(VIII)	6	Hexane	91,0	62–64 Pentane	0,66	53,11 / 52,94	3,52 / 3,43	– / –	27,58 / 27,94	$C_9H_7F_3O_3$

*n_D^{20} 1.4690.

TABLE 2. ^1H and ^{19}F NMR Spectra of (II)-(VII)*

Compound	Chemical shifts δ, ppm (J, Hz)							
	^1H					^{19}F **		
	H^2	H^3	H^4	H^5	H^6	CF_3	CF_2	
							F^A	F^B
(II)	–	–	–	6,90 d	6,60 d	–	–	–
				(8,5)				
(III)	–	7,32 br.d	6,55 d.d	–	6,33 br.d	–3,25	+13,46	+15,98
		(8,5)					(167,59)	
			(2,0)				(7,53)	
							(11,09)	
(IV)	–	6,70 s	–	–	6,30 s	–3,20	+12,90	+16,00
							(164,57)	
(V)	–	7,74 br.s	–	–	6,65 s	–3,33	+13,00	+16,23
							(168,43)	
							(7,50)	
							(11,23)	
						–1,55 c		
(VI)	–	7,82 br.d	6,80 d.d	–	6,62 br.d	–3,52	+13,00	+15,84
		(8,5)					(167,78)	
			(2,0)				(7,53)	
							(11,20)	
(VII)	6,53	–	–	7,44 d	6,60 d.d	–4,44	+12,00	+15,54
				(9,0)			(167,83)	
		(2,5)					(7,49)	
							(11,23)	

*The spectra of (II) and (V) were taken in acetone-d_6, while the spectrum of (IV) was taken in methanol-d_4 and the spectra of the other compounds were taken in $CDCl_3$.
**The CF_3 and CF_2 groups in the spectra of these compounds appear as ABX_3 systems.

However, O-alkylation products were also detected in the reaction mixture in these cases by ^{13}C and ^{19}F NMR spectroscopy. The C-alkylation of phenols is achieved under more vigorous conditions with decreasing donor properties of the meta substituents. Thus, NPFA reacts with m-cresol in CCl_4 at 100°C over 3 h to give adduct (VI) only in 37% yield.

Of the methyl ethers of halophenols, cresols, and phenol and the totally methylated pyrocatechol, hydroquinone, pyrogallol, and resorcin, only the latter reacts with NPFA at 20°C to give 1,3-dimethoxy-4-(1-hydroxy-2-nitropentafluoroisopropyl)benzene (VII) in quantitative yield after six days.

The product phenols (II)-(VI) are colorless, crystalline compounds, which are stable upon storage. These compounds decompose to give difluoronitromethane and o-trifluoroacetylphenol upon heating in aqueous alkali or in a solvent in the presence of activated charcoal. This behavior is characteristic for other adducts of NPFA with nucleophiles [5]. Heating (III) in hexane at reflux leads to its quantitative conversion to (VIII) as indicated by thin-layer chromatography.† The mild reaction conditions, high yields of the starting and desired reagents, and low boiling point of difluoronitromethane indicate that this is a convenient synthetic pathway for the selective preparation of o-trifluoroacetyl derivatives of polyphenols.

EXPERIMENTAL

The ^{13}C, ^{1}H, and ^{19}F NMR spectra of the compounds synthesized were taken in acetone, acetone-d_6, methanol-d_4, and $CDCl_3$ on a Bruker 200SY spectrometer at 50.31, 200.13, and 188.30 MHz, respectively. The chemical shifts were determined for the ^{13}C and ^{1}H NMR spectra relative to TMS as the internal standard and for the ^{19}F NMR spectra relative to CF_3CO_2H as the external standard. The R_f values are given for Kavalier Silufol-254 plates (manufactured in Czechoslovakia) using 1:3 acetone–CCl_4 as the eluent. The compounds were detected by UV light. The synthesis conditions and indices of the compounds are given in Table 1, while the spectral characteristics are given in Table 2.

2,3-Dihydroxy-4-(1-hydroxy-2-nitropentafluoroisopropyl)phenol (II). A mixture of 1.26 g pyrogallol, 5 ml anhydrous nitromethane, and 1.93 g NPFA was maintained for 12 h at 20°C. The solvent was evaporated to give 3.0 g pure crystalline (II). ^{13}C NMR spectrum (δ, ppm): 146.41, 144.77 (C^1, C^3), 132.41 (C^2), 121.86 (CF_3, J_{C-F} = 286.00 Hz), 120.55 (CF_2, J_{C-F} = 295.00 Hz), 117.51 (C^5), 107.13 (C^6), 106.22 (C^4), 79.43 (C^*–CF_3).

Products (III)-(V) and (VII) were obtained by analogy.

5-Methyl-2-(1-hydroxy-2-nitropentafluoroisopropyl)phenol (VI). A mixture of 1.08 g m-cresol, 1.93 g NPFA, and CCl_4 was heated for 3 h in a sealed ampul at 90-100°C and cooled. The solvent was removed and the residue was recrystallized from hexane to give 1.1 g pure (VI).

5-Methoxy-2-trifluoroacetylphenol (VIII). A solution of 3.17 g (III) in 20 ml hexane was heated at reflux for 6 h with 0.5 g activated charcoal. The mixture was filtered off and the sovlent was removed. The residue was crystallized from pentane to give 1.86 g crystalline (VIII). ^{13}C NMR spectrum in CCl_4 (δ, ppm): 180.31 (C=O, J_{C-F} = 35.00 Hz), 166.21, 165.93 (C^1, C^5), 130.06 (C^3), 114.76 (CF_3, J_{C-F} = 287.50 Hz), 107.36 (C^4), 106.00 (C^2), 98.91 (C^6), 53.36 (OCH_3).

CONCLUSIONS

The reaction of nitropentafluoroacetone with phenols leads to O-alkylation products (hemiketals), which are transformed in the case of phenols with enhanced C-nucleophilicity, to ortho-alkylation products.

LITERATURE CITED

1. V. I. Dyachenko, A. F. Kolomiets, and A. V. Fokin, Izv. Akad. Nauk SSSR, Ser. Khim., 1080 (1987).
2. V. I. Dyachenko, A. F. Kolomiets, and A. V. Fokin, Izv. Akad. Nauk SSSR, Ser. Khim., 2511 (1987).

†See Experimental.

3. A. V. Fokin, A. I. Rapkin, and V. A. Komarov, Izv. Akad. Nauk SSSR, Ser. Khim., 1785 (1982).
4. L. A. Simonyan, Candidate's Dissertation in the Chemical Sciences, Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow (1968).
5. N. P. Gambaryan, E. M. Rokhlina, and Yu. V. Zeifman, Izv. Akad. Nauk SSSR, Ser. Khim., 1466 (1965).